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Title of Thesis: REACTIVITY OF BENZYLCHROMIUM(III) DERIVATIVES
AND IRON COMPLEXES OF TIRON AND ASCORBATE

Degree: DOCTOR OF PHILOSOPHY

Year this Degree Granted: 1996

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REACTIVITY OF BENZYLCHROMIUM(III) DERIVATIVES AND
IRON COMPLEXES OF TIRON AND ASCORBATE

BY

ZHONGSHENG ZHANG



A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta

Spring, 1996

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Reactivity of Benzylchromium(III) Derivatives and Iron Complexes of Tiron and Ascorbate submitted by Zhongsheng Zhang in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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To my family and parents

Abstract

The kinetics of heterolysis and homolysis have been studied for $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ and derivatives in 0.01–0.95 M HClO_4 . The rate of heterolysis has terms first order and independent of $[\text{H}^+]$ and is catalyzed by sulfate ion. The homolysis reaction was studied in the presence of several oxidizing scavengers. It was found that the rate is independent of the nature and concentration of the scavenger, but the organic products vary considerably with the nature of the scavenger and the substituent on the benzyl ligand. For several systems, with aqueous iron(III) as scavenger, the products show competition between oxidation to form the alcohol and radical dimerization to give the bibenzyl derivatives.

The kinetics of the heterolysis of the 2-cyano, 3-cyano, 4-cyano and parent benzyl complexes of pentaquachromium(III) have been studied in phosphate, methyl phosphate and acetate buffers. The results indicate that the conjugate bases of the buffer species form mono complexes with the chromium(III) species, and the complex formation constants correlate with the $\text{p}K_a$ of the parent acid. Species with an ionizable proton are much more reactive than the fully deprotonated species. Acetate ion causes the rate of homolysis to increase by factors of 1.5–2.5 for the benzyl and 3-cyano and 4-cyano systems but causes a reduction in rate for the 2-cyano complex.

The kinetics of dissociation of the mono-, bis- and tris-Tiron complexes of iron(III) have been studied in acidic aqueous solutions, as a function of $[\text{H}^+]$ and temperature. The dissociation constants, formation constants and activation parameters have been determined. From the variation in rate constants and activation parameters, it is suggested that the bis and tris complexes undergo substitution by dissociative activation.

The kinetics of the oxidation of iron(II)-Tiron and iron(II)-ascorbate complexes has been studied at pH 3.8-7.5. The oxidation of the bis-iron(II) complexes provides the dominant pathway. The variation of the rate constant with pH is mainly due to the Fe(L)(LH)^- complex for Tiron, and the Fe(L)_2^{2-} complex for ascorbate. Finally, the iron(III)-ascorbate solid is isolated and the structure is suggested.

Acknowledgments

I would like to express my gratitude to my supervisor, Professor Robert B. Jordan for his advice, encouragement and thoughtfulness during the course of my studies, and for his assistance in the preparation of this thesis.

I dedicated this thesis partially to my wife, Yanni, for her love, understanding and encouragement.

I want to thank my parents, especially my mother-in-law, Yufang, for her taking care of my son during my years of study.

I would like to thank my friends and colleagues, Dr. Margaret Sisley and Kefei Wang for their friendship and frequent helpful discussions.

Financial assistance from the University of Alberta is gratefully acknowledged.

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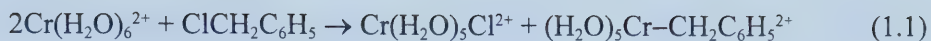
Chapter 1. Introduction

Chemistry of Organochromium(III) Complexes

Chromium(III) forms a large series of organometallic complexes with the general formula $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. The R may be any aliphatic or benzylic group and is σ bonded through the α -carbon to the metal.¹ Chromium complexes containing several organic groups such as $\text{R}_3\text{Cr}(\text{THF})_3$, $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$, have been prepared in non-aqueous solvents,² but they are much less stable in water than $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes.

Preparation and Formation Mechanism. There are several ways to synthesize $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes. These include the reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with organic halides, organic peroxides, modified Fenton's reagent, and photolysis of alkyl compounds in the presence of aqueous chromium(II). All of these methods are aimed at producing the desired carbon-centred radical ($\text{R}^\bullet$), which then reacts with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ to produce organochromium(III) complexes, i.e. $\text{Cr}(\text{H}_2\text{O})_6^{2+} + \text{R}^\bullet \rightarrow (\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. The method of choice is dictated generally by the kinetic stability of the product.

$\text{Cr}(\text{H}_2\text{O})_6^{2+}$ reaction with organic halides. If the $\text{R}-\text{X}$ bond of organic halides is not strong and the final $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complex is relatively stable, then mixing $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with the organic halide gives a simple way to synthesize these chromium complexes. Benzyl halide,³ polyhaloalkanes⁴ and ICH_2CN ⁵ are suitable for this preparation. Anet and Leblanc⁶ prepared and characterized benzylpentaquachromium(III), which was the first organoaquachromium(III) complex, by mixing benzylchloride and chromium(II). They found the following reaction:

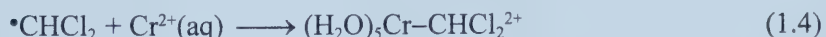


Mono-substituted alkyl halides fail to react with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ in aqueous solution. However, complexation of chromium(II) by macrocyclic ligands, such as [14]aneN₄ (or 1,4,8,11-tetraazacyclotetradecane) and [15]aneN₄ (or 1,4,8,12-tetraazacyclopentadecane) reduces the $\text{Cr}^{3+/2+}$ potential from -0.41 V to -0.58 and -0.86 V, respectively, leading to ready reaction with alkyl halides.^{7,8}

The first indication of the mechanism of these reactions came from the study by Anet⁹ of the reduction of chloroform by chromous perchlorate in aqueous solution. It was found that the reaction yields equal amounts of chloropentaaquochromium(III) perchlorate and dichloromethylpentaaquochromium(III) perchlorate. The former product makes the reaction appear analogous to the first inner-sphere reaction characterized by Taube and Myers,¹⁰ as shown in eq 1.2. Anet proposed that the

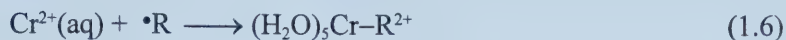
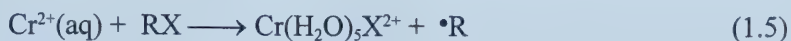


reduction of chloroform proceeds in a similar fashion, with transfer of a chlorine atom from carbon to chromium, then dichloromethyl radicals will be formed and react with another chromous ion to give an organochromium ion as follows:



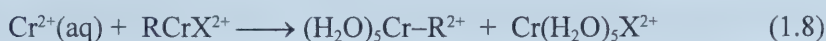
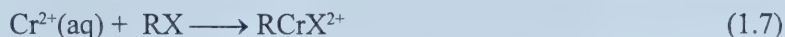
Kochi and Davis^{3a} suggested that benzylpentaaquachromium(III) was formed by the same mechanism.

This mechanism may be generalized as shown by the following two reactions. The first step (eq 1.5) is halogen atom abstraction to produce the free radical ($\bullet R$)

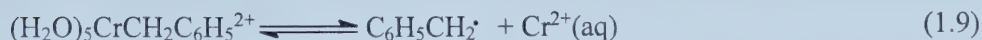


and $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$. Then $\bullet\text{R}$ is reduced by $\text{Cr}^{2+}(\text{aq})$ to give the organochromium(III) product. The formation of the halogen complex, $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$, is strong evidence for this mechanism since $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ is not formed from the $\text{Cr}^{2+}(\text{aq})$ and X^- under the conditions of these reactions.

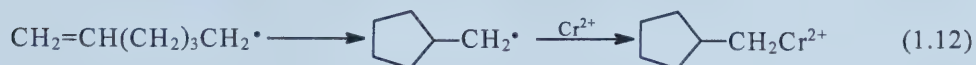
An alternative oxidative addition mechanism is shown in eq 1.7–1.8. This has been excluded by the identification of the radical intermediate in eq 1.5. Kochi and



Davis^{3a} employed acrylonitrile to trap the benzyl radical intermediate in eq 1.5, and identified the expected product $\text{C}_6\text{H}_5(\text{CH}_2)_3\text{CN}$. Nevertheless, this trapping reaction does not provide definitive evidence for the radical in eq 1.5 if the product $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ undergoes homolysis and then reacts with acrylonitrile as in the following reactions:



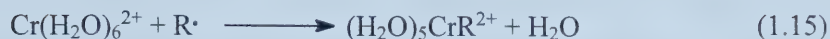
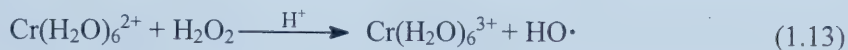
More definitive evidence for the radical intermediate in eq 1.5 has been demonstrated by Kochi et al.¹¹ and Espenson et al.⁸ from the reaction of 6-bromo-1-hexene with Cr(en)^{2+} and $\text{Cr}([\text{15}] \text{aneN}_4)^{2+}$. It was found that the cyclopentylmethyl-chromium(III) complex is formed, as expected from the cyclization of the initial radical as shown in the following reaction.



The rate of the halogen atom abstraction in eq 1.5 depends on the energy of the R-X bond and on the substituents on the α -carbon. For a given alkyl group,^{3a} the halides react in the order $\text{I} > \text{Br} > \text{Cl}$. For example, the rate constant of eq 1.5 is $3.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for benzyl chloride, $0.41 \text{ M}^{-1} \text{ s}^{-1}$ for benzyl bromide and $1.8 \text{ M}^{-1} \text{ s}^{-1}$ for benzyl iodide. For a given halide, the trend of rate constants is tertiary > secondary > primary in accord with the stabilization of the free radical intermediate.¹² Kochi et al.^{3a} studied the variation of the rate constant of eq 1.5 with substituents on benzyl halides. They found that all substituents increase the rate relative to the unsubstituted compounds, whether the substituents are electron-withdrawing or electron-donating groups.

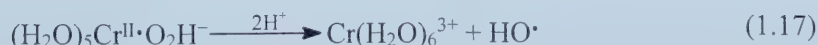
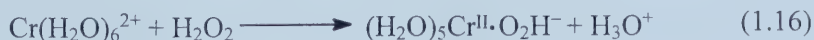
$\text{Cr}(\text{H}_2\text{O})_6^{2+}$ reaction with modified Fenton's reagent. Since the halogen atom abstraction in eq 1.5 is the rate controlling step, the synthesis of $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ from organic halide may not be possible if the complex decomposes rapidly. The modified Fenton reagents provide a much faster way to produce the $\text{R}\cdot$ radical. A hydroxyl radical is generated by reaction 1.13 and then hydrogen atom abstraction

from the reactant RH yields the $R^\bullet$ radical (eq 1.14) which in turn reacts with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ to give the desired product (eq 1.15).



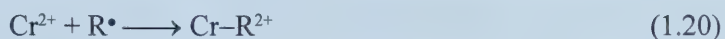
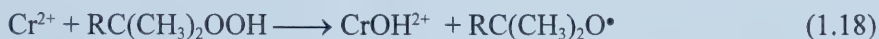
Rate constants for eq 1.13, 1.14 and 1.15 for alcohols are $7.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$,¹³ $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively.¹⁴ Since eq 1.13 is still the rate controlling step, this technique is only used for the study of chromium complexes with a half-life for decomposition longer than 50 ms. One limitation of this method is that RH must be sufficiently soluble in the solvent so that it competes effectively with Cr^{2+} for the hydroxy radical. Another problem is that the reaction may produce mixtures of complexes that may confuse the interpretation of results from *in situ* preparations.

The modified Fenton reaction has been used for the preparation of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes^{15,16} and macrocyclic analogues¹⁷ with $\text{R} = \text{CH}_2\text{OH}$, $\text{CH}(\text{CH}_3)\text{OH}$ and CH_2OCH_3 , but it failed for $\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$, due to fast homolysis of $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})\text{Cr}(\text{CH}_3)_2\text{COH}^{2+}$. Espenson and co-workers^{18a} pointed out that eq 1.13 is a sum of two reactions which includes the formation of a transient complex $(\text{H}_2\text{O})_5\text{Cr}^{\text{II}}\cdot\text{O}_2\text{H}^-$ in eq 1.16 and decomposition in eq 1.17. The latter equation is suggested as a rate controlling inner-sphere electron transfer reaction by Gaede and van Eldik,^{18b} so that in the modified Fenton reaction, eq 1.17 is the rate controlling step.

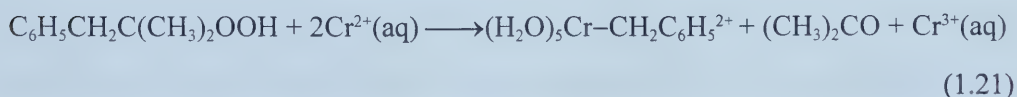


Espenson et al.^{18a} confirmed that the reaction between $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and H_2O_2 in acidic conditions actually is a "Fenton-like" reaction in the presence of the organic substrates. This is different from the $\text{Cu}(\text{I})$ transient complex $(\text{H}_2\text{O})_m\text{Cu}^+\cdot\text{O}_2\text{H}^-$ that reacts with the organic substrates directly without forming $\text{HO}^\bullet$.

$\text{Cr}(\text{H}_2\text{O})_6^{2+}$ reaction with peroxides. Hydroperoxides $\text{RC}(\text{CH}_3)_2\text{OOH}$ or peroxides $(\text{RCOO})_2$ will dissociate to $\text{R}^\bullet$ radical by thermolysis, photolysis or reaction with Cr^{2+} . The reaction is considered to proceed by the following mechanism, in which the first step is rate-controlling.¹

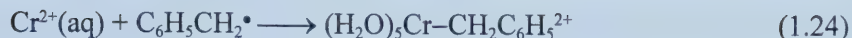


Using this method, $(\text{H}_2\text{O})_5\text{Cr-CH}_2\text{C}_6\text{H}_5^{2+}$ has been made by quantitatively reacting α,α -dimethyl- β -phenethyl hydroperoxide with Cr^{2+} , as shown in eq 1.21. The reduction of



this hydroperoxide by Cr^{2+} was instantaneous at 0°C and produced acetone in the predicted amount.^{3a,11b,11c} The fragmentation of α,α -dimethyloxy- β -phenethoxy radical in eq 1.19 is known to be rapid.¹⁹ Similarly, the benzylchromium(III) complex can be prepared by reduction of bisphenylacetyl peroxide as shown in the following reactions:²⁰



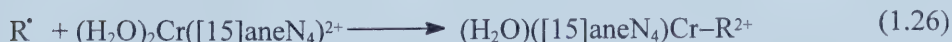


For $\text{RC}(\text{CH}_3)_2\text{OOH}$, the nature of the R group has very little effect on the rate of reduction in eq 1.18 and the rate constants span a narrow range of $(1-6) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C because the OH group attacked by Cr^{2+} is far away from the R group.¹

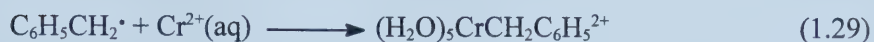
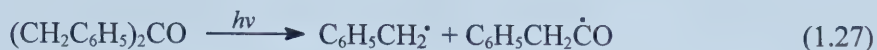
The limitation of this method is that the fragmentation of $\text{RC}(\text{CH}_3)_2\text{O}\bullet$ in eq 1.19 must be finished before it reacts with Cr^{2+} or solvents to produce $\text{RC}(\text{CH}_3)_2\text{OH}$ and other undesired products.^{11c}

Photolysis. Organic radical generation is the rate controlling step in the halogen atom abstraction and modified Fenton reactions. Much faster radical production can be achieved by flash photolysis of appropriate substrates. These methods are suitable both for the preparation of chromium complexes and for the evaluation of the colligation rate between the alkyl radical and Cr^{2+} .

The chromium(II) complex of the macrocycle ($[\text{15}] \text{aneN}_4$) reacts with alkyl radicals which are generated from the photolysis of alkyl cobalt(III) complexes, such as $\text{RCo}(\text{dmgH})_2$ and $\text{RCo}([\text{14}] \text{aneN}_4)$, to produce the alkyl chromium(III) complex and the colligation rate between chromium(II) and alkyl radicals can be determined.^{17a} The reaction is viewed as cleavage of the Co–C σ bond in which radical $\text{R}\bullet$ is captured by $(\text{H}_2\text{O})_2\text{Cr}([\text{15}] \text{aneN}_4)^{2+}$, as shown in eq 1.25–1.26.



Photolysis of dibenzyl ketone in the presence of Cr^{2+} can be used to prepare the benzyl chromium complex and determine the colligation rate as shown in the following reactions.²¹ The experimental results showed that the photodecarbonylation

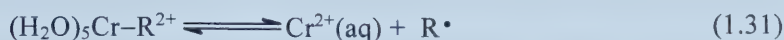
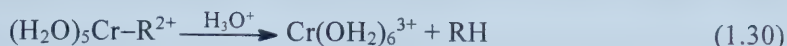


rate constant of dibenzyl ketones is 10^8 s^{-1} and the $(\text{H}_2\text{O})_5\text{CrCOCH}_2\text{C}_6\text{H}_5^{2+}$ complex is not found.^{21,22}

Using tetramethylpiperidine-1-oxyl radical  to trap the radical at a diffusion controlled rate, -O- $\text{CH}_2\text{C}_6\text{H}_5$ and -O-CO $\text{CH}_2\text{C}_6\text{H}_5$ were obtained.

The latter formation proves photodecarbonylation proceeds *via* eq 1.27 involving the formation of the phenylacetyl radical exclusive of a solvent cage.²² Photolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ results in $\text{Cr}^{2+}(\text{aq})$ and $^\bullet\text{CH}_2\text{C}_6\text{H}_5$ which will re-form $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$. The re-formation rate constant ($8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) after photolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ is equal to that determined by photolysis of dibenzyl ketone.²³ The consistent rate constant of re-formation in both methods indicates that there are no substantial solvent cage effects on $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ formation. Further studies reveal that all re-formation rate constants are at $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and no steric effect of the R group was found.^{16,23}

Decomposition Mechanism of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. Organopentaaquachromium(III) complexes in aqueous solution were shown to decompose *via* heterolysis (eq 1.30) and homolysis (eq 1.31). The addition of aqueous chromium(II) suppresses the initial

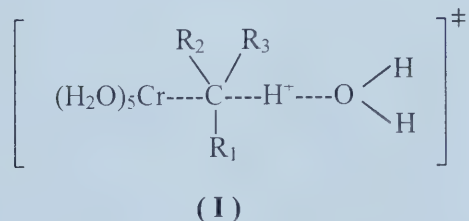


homolysis equilibrium and allows the heterolysis reaction to be studied. Homolysis is promoted by the addition of scavengers for chromium(II) and /or $\text{R}^\bullet$. Recently, some alkylchromium(III) complexes, such as $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})\text{Cr}-\text{CH}(\text{CH}_3)_2^{2+}$, have been found to decompose by β -hydrogen elimination, as well as by homolysis.

Heterolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. Generally, the rate law for decomposition of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ by heterolysis has two terms, as shown by eq 1.32. When the measurements were carried out in D_2O instead of H_2O , it was found that both k_0 and k_1

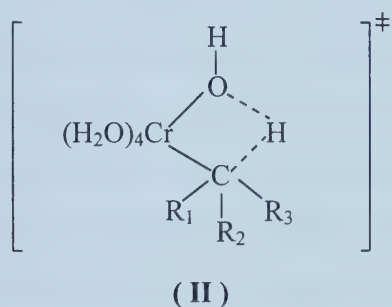
$$-\text{d}[(\text{H}_2\text{O})_5\text{CrR}^{2+}]/\text{d}t = (k_0 + k_1[\text{H}^+])[(\text{H}_2\text{O})_5\text{CrR}^{2+}] \quad (1.32)$$

have large kinetic H/D isotope effects.²⁴ For the acid-dependent term (k_1), the transition state in structure **I** is commonly accepted. Then the mechanism involves

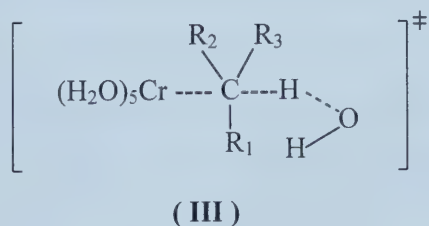


H_3O^+ electrophilically attacking the α -carbon atom. The electrophilic reactions of chromium complexes have been observed for other good electrophilic reagents,¹ such as Hg^{2+} , CH_3Hg^+ and Br_2 .

It is argued that the acid-independent term k_0 results from attack of either a *cis*-water ligand or the solvent water on the α -carbon atom. It was suggested that the attacking water molecule is the ligand bound to the chromium, as shown in structure **II**, because the water ligand is a stronger acid than the solvent water, and no steric effect of bulky R_1 and R_2 substituents is observed.¹ The observed volumes of activation ΔV^* of essentially zero for k_0 in $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}(\text{CH}_3)_2\text{OH}^{2+}$ and $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}(\text{CH}_3)_2^{2+}$ are also consistent with structure **II**, in which the transition state would involve no net development of charge.²⁵

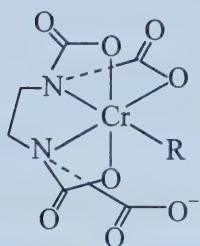


On the other hand, it was proposed that the transition state for the acid-independent term k_0 is analogous to that of the acid-dependent term, i.e. the solvent water molecule attacking the α -carbon atom of alkyl ligands, as shown in structure **III**.

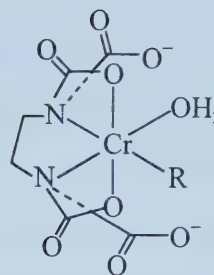


Rotman et al.²⁶ pointed out that *cis*-H₂O ligands are not necessary since the k_0 values for *trans*-[([15]aneN₄)(H₂O)Cr-C(CH₃)₂OH]²⁺ ($2.0 \times 10^{-3} \text{ s}^{-1}$) and the parent pentaqua complex ($3.3 \times 10^{-3} \text{ s}^{-1}$) are similar. However, these observations are now in doubt due to the more recent observation of Espenson et al.^{17a} that *trans*-[([15]aneN₄)(H₂O)Cr-C(CH₃)₂OH]²⁺ could not be isolated due to its rapid homolysis. For the analogous complexes [([15]aneN₄)(H₂O)Cr-R]²⁺ with R = CH₂OH and CH₂OCH₃, Espenson et al.^{12b,17} found that the macrocyclic complexes are completely stable toward heterolysis under conditions where their pentaqua counterparts readily react. Espenson et al. suggested that the electrophilic agent is the *cis*-coordinated water in the [(H₂O)₅Cr-R]²⁺ complexes, and this agent is absent in the macrocyclic complex. Rotman et al.²⁶ and Ogino et al.²⁷ also have argued in favor of solvent water as the electrophile because the k_0 of [(EDTA)Cr-R]²⁻ is similar to that of [(H₂O)₅Cr-R]²⁺. This argument assumes that the structure of [(EDTA)Cr-R]²⁻ is as shown in **IV** and lacks a *cis*-coordinated water. Espenson¹ suggested that the EDTA complex may, by hydrogen bonding, utilize a water molecule in the second coordination sphere. It is also possible that the EDTA ligand may weaken the Cr-R bond so that the comparison of k_0 between [(EDTA)Cr-R]²⁻ and [(H₂O)₅Cr-R]²⁺ is inappropriate. Another complication is that EDTA may be only quadridentate and the complex may have a *cis*-coordinated water as in **V**.

Espenson and co-workers^{12b,17} found that the acid-dependent term k_1 in *trans*-[([15]aneN₄)(H₂O)Cr-R]²⁺ complexes also is smaller than that in (H₂O)₅Cr-R]²⁺. They attributed the slowness of electrophilic attack of H₃O⁺ on the macrocycles to the steric repulsion from the ligand as H₃O⁺ approaches the α -carbon atom. Another model suggested by Jordan et al.²⁸ for benzylchromium complexes is shown in Scheme I. The *cis*-water and protonated *cis*-water exist in equilibrium and the k_1 term may be



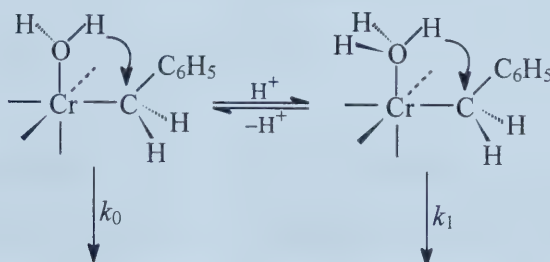
(IV)



(V)

mainly from *cis*-H₃O⁺ attack at the α -carbon atom. The macrocycle complexes with no *cis*-H₃O⁺ lose this contribution.

Scheme I

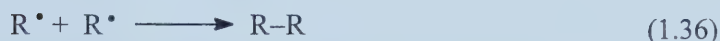
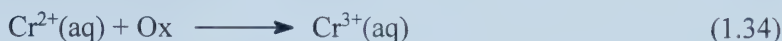
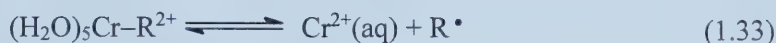


Homolysis of (H₂O)₅Cr-R²⁺. The (H₂O)₅Cr-R²⁺ complexes can undergo homolysis to Cr²⁺(aq) and R[•] radical. The equilibrium constants for eq 1.31 are 6.5×10^{-13} and 5.9×10^{-12} M for ([15]aneN₄)(H₂O)Cr-R²⁺ with R = CH₂C₆H₅ and CH(CH₃)₂^{12b,17a,26} and 3.1×10^{-11} M for the benzylchromium complex.^{21,29}

The transition state for homolysis can be represented as [(H₂O)₅Cr²⁺...R]^{*} or the reaction can be viewed as electron transfer from ligand to chromium. The negative value of the Hammett constant ρ for these reactions indicates that electron-donating substituents accelerate homolysis.²⁹ This suggests that the alkyl carbon is stabilized in

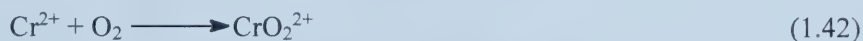
the transition state relative to the ground state by increasing electron density or electron-donating substituents favor this electron transfer from R^- to Cr^{3+} .

The addition of mild oxidizing scavengers (Ox) to remove $Cr^{2+}(aq)$ and/or $R^\bullet$ will promote the homolysis as shown in eq 1.33–1.36. The oxidizing scavengers such as Co(III) complexes, $Fe^{3+}(aq)$, $Cu^{2+}(aq)$, H_2O_2 and O_2 have been used in homolytic kinetic studies.^{29–31}



Generally, the homolysis in eq 1.33 is the rate controlling step. The homolytic rate constant is independent of the type and concentration of the oxidant scavengers, but is quite dependent on the R group. The scavenger (Ox) will oxidize $Cr^{2+}(aq)$ to $Cr^{3+}(aq)$ (eq 1.34) and/or oxidize the radical to organic products (eq 1.35), depending on the nature of the scavenger and the R group. In addition, the $R^\bullet$ can dimerize to $R-R$ (eq 1.36).

The reaction mechanism of $(H_2O)_5Cr-CH(CH_3)_2^{2+}$ with oxygen has been studied and a chain mechanism has been proposed, as shown in eq 1.37–1.42.³² From eq 1.40 and 1.41, final organic products are ketone and a lesser amount of alcohol. The kinetics of this chain reaction follow a complex rate law (eq 1.43) that can be derived from a steady state approximation for the radical intermediates. Further evidence for this special mechanism is that the decomposition of $CrCH(CH_3)_2^{2+}$ has a half-time



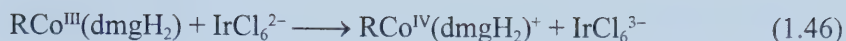
$$\text{rate} = k_{37}[\text{Cr}-\text{CH}(\text{CH}_3)_2^{2+}] + k_{39}(k_{37}/2k_{40})^{3/2}[\text{Cr}-\text{CH}(\text{CH}_3)_2^{2+}]^{3/2} \quad (1.43)$$

of a few minutes with O_2 compared to about 1 hour with other scavengers. However, if the O_2 concentration is low, the peroxy radical might recombine with its parent Cr^{2+} before the latter reacts with a second O_2 , so that the reaction $\text{ROO}\cdot + \text{Cr}^{2+} \longrightarrow \text{ROOCr}^{2+}$ could be competitive with eq 1.42. In this case, no chain reaction occurs and the decomposition rate is the same for all scavengers.

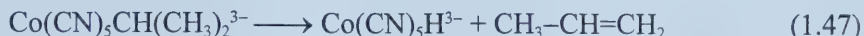
Strong oxidizing agents, such as HNO_2 , $\text{Ni}([\text{14}] \text{aneN}_4)^{3+}$, $\text{Ni}([\text{9}] \text{aneN}_3)_2^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$, can directly oxidize the $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ by the following reactions.³³ The



rate-controlling one-electron transfer yields a short-lived $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{3+}$ complex, which decomposes by homolysis (R = alkyl, benzyl) or by intramolecular electron transfer (R = alkoxyalkyl) (not shown in above reaction). Similar oxidative homolysis has been found in some cobalt(III) complexes, as in the following.³⁴



β -Elimination. No β -hydrogen elimination has been observed for $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes, although $\text{Co}(\text{CN})_5\text{CH}(\text{CH}_3)_2^{3-}$ undergoes β -hydrogen elimination as follows.³⁵

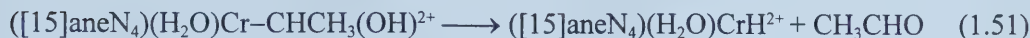
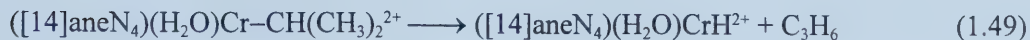


However, β -OH (eq 1.48) and β -halogen elimination have been observed for alkylchromium complexes.³⁶



The absence of β -hydrogen elimination for $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes may be due to the instability of $(\text{H}_2\text{O})_5\text{CrH}^{2+}$, while the formation of stable $(\text{H}_2\text{O})_5\text{CrBr}^{2+}$ and $(\text{H}_2\text{O})_5\text{CrOH}^{2+}$ species favor the β -OH and β -halogen elimination. If the intermediate $(\text{H}_2\text{O})_5\text{CrH}^{2+}$ is stabilized by chelating ligands, the β -hydrogen elimination may be observed. Thus $([\text{14}] \text{aneN}_4)(\text{H}_2\text{O})\text{CrCH}(\text{CH}_3)_2^{2+}$ and $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})\text{Cr}-\text{CHCH}_3(\text{OH})^{2+}$ show a β -hydrogen elimination pathway, which accompanies the homolysis, as shown in eq 1.49–1.52.^{12,17} For $\text{L}(\text{H}_2\text{O})\text{Cr}-\text{R}^{2+}$ ($\text{L} = [\text{14}] \text{aneN}_4$ and $[\text{15}] \text{aneN}_4$), electron donation from the N_4 macrocycle stabilizes the $\text{Cr}(\text{III})$ state. The size of the electronic effect of the ligands L becomes obvious if one compares the reduction potential for $([\text{14}] \text{aneN}_4)(\text{H}_2\text{O})_2\text{Cr}^{3+/2+}$ (-0.86 V), $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})_2\text{Cr}^{3+/2+}$ (-0.58 V) and $\text{Cr}(\text{H}_2\text{O})_6^{3+/2+}$ (-0.41 V).^{7,8} If we view that the hydrido complex, $(\text{H}_2\text{O})_5\text{CrH}^{2+}$ as the simplest member of the alkylchromium cations, then $\text{L}(\text{H}_2\text{O})\text{CrH}^{2+}$

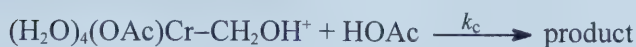
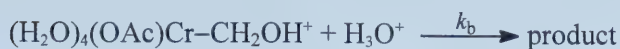
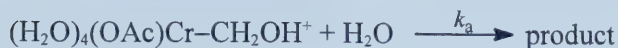
could be more stable than $(\text{H}_2\text{O})_5\text{CrH}^{2+}$, and the β -hydrogen elimination of $\text{L}(\text{H}_2\text{O})\text{Cr}-\text{R}^{2+}$ can be rationalized.



In general, β -elimination reactions of alkylchromium complexes will be favored if CrX^{2+} is relatively stable and the (β -)carbon-X bond is not too strong. Furthermore, if a chelating ligand (L) makes $\text{Cr}(\text{III})$ in $\text{L}(\text{H}_2\text{O})\text{Cr}-\text{R}^{2+}$ more stable, then the homolysis is retarded and β -hydrogen elimination may become a significant decomposition pathway.

Anion Catalysis of Decomposition of Chromium Complexes. Kochi and Buchanan³⁷ observed that acetate catalyses the decomposition of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$. However, the effects of added ions on the rates of Cr-C bond cleavage have not been investigated extensively, and the mechanism is not well understood. Ogino and co-workers³⁸ found that addition of acetate to a solution of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$ causes a remarkable acceleration of the rate of the heterolysis reaction. They interpreted their kinetic data in terms of a rapid formation of $(\text{H}_2\text{O})_4(\text{OAc})\text{Cr}-\text{CH}_2\text{OH}^+$ (formation constant K_f of $11 \pm 1 \text{ M}^{-1}$ at 25°C) followed by an acetic acid induced heterolysis reaction of this complex. This pathway was found to be 1600 times faster than the heterolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$. The reaction scheme is shown in Scheme II.

Scheme II



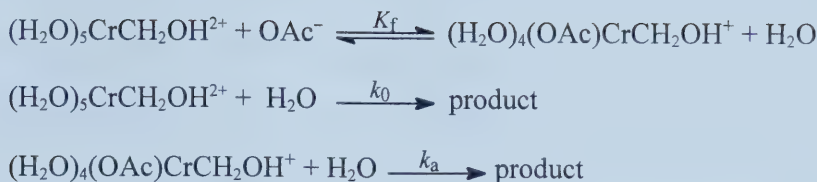
The pseudo-first-order rate constant is given by the following equation, where K_a is the acid dissociation constant of acetic acid.

$$k_{\text{obsd}} = \frac{1}{K_f[\text{OAc}^-] + 1} \left\{ k_a K_f [\text{OAc}^-] + k_b K_f [\text{H}^+] [\text{OAc}^-] + \frac{k_c K_f [\text{H}^+] [\text{OAc}^-]^2}{K_f} \right\} \quad (1.53)$$

Cohen et al.³⁹ performed a systematic kinetic study as a function of acetate concentration, temperature, and pressure for a series of complexes of the type $\text{LCr}-\text{CH}_2\text{OH}^{2+}$, with $\text{L} = \text{H}_2\text{O}$, nta (or nitrilotriacetate), and $[\text{15}] \text{aneN}_4$, in order to determine the activation parameters for the acetate-catalysed reaction. The results of this study suggest a dissociatively activated heterolysis process involving an interchange ligand substitution reaction with a solvent molecule.

It must be noted that different groups have assigned different mechanisms to the acetate catalysed decomposition of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$. Ogino et al.³⁸ found that k_c was the dominant pathway and assigned this to rapid formation of $(\text{H}_2\text{O})_4(\text{OAc})\text{Cr}-\text{CH}_2\text{OH}^+$ followed by attack of acetic acid. However, this term was not observed by van Eldik et al.^{40,41} and Meyerstein et al.⁴² They proposed the reactions in Scheme III.

Scheme III

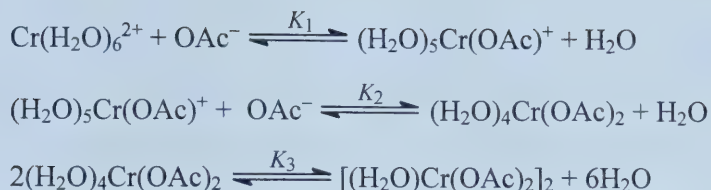


This gives the following rate law

$$k_{\text{obsd}} = \frac{k_0 + k_a K_f [\text{OAc}^-]}{1 + K_f [\text{OAc}^-]} \quad (1.54)$$

that simplifies to $k_{\text{obsd}} = k_0 + k'[\text{OAc}^-]$ at low acetate concentration. Even though all these groups employed the modified Fenton's reagent to prepare $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$, the addition of acetate was done differently. Ogino et al.³⁸ separated $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$ from the reaction mixture on the ion exchange column and studied the accelerating heterolysis by adding acetate to purified $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$. However, acetate was added to the $\text{Cr}^{2+}(\text{aq})$ solution prior to the formation of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$ by van Eldik et al. and Meyerstein et al.³⁹⁻⁴¹ and the heterolysis reaction was studied *in situ*. It is known that $\text{Cr}^{2+}(\text{aq})$ undergoes complex formation with acetate ions in aqueous solution according to Scheme IV,⁴² in which $K_1 = 15 \text{ M}^{-1}$, $K_2 = 5 \text{ M}^{-1}$, and $K_3 = 2.2 \times 10^4 \text{ M}^{-1}$. Therefore the *in situ* method could produce mixtures of $[(\text{H}_2\text{O})_{5-n}(\text{CH}_3\text{CO}_2)_n\text{Cr}-\text{CH}_2\text{OH}]^{2-n}$ even though the dimeric species may not be formed.^{39,43} Very recently, van Eldik et al.⁴⁴ studied the phosphate acceleration of heterolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ ($\text{R}=\text{CH}_2\text{OH}$ and $\text{C}(\text{CH}_3)_2\text{OH}$) at $\text{pH} \approx 3.2$ and found that *in situ* heterolysis was almost a factor of 2 larger than the reaction in which phosphate was added to Cr^{2+} solution after the formation of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. They accounted for this apparent difference on the basis of the pH difference between these two

Scheme IV



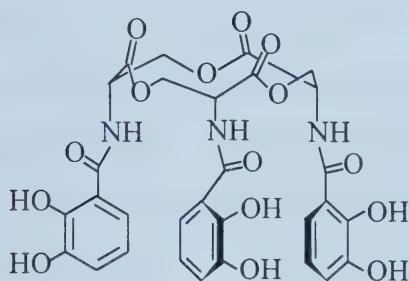
procedures. If the experiments were performed at $\text{pH} \approx 2$, one could avoid the pH change because H_2PO_4^- is a buffer in this region. Cohen and Meyerstein⁴¹ studied the acetate effect in the presence of two chelating ligands nta and [15]aneN₄. They found no significant effect of acetate in the presence of nta, but a very significant effect for the [15]aneN₄ complex, similar to that observed for the aqua system. From this, they concluded that acetate must occupy the site *trans* to the Cr–C bond in order to induce the heterolysis reaction. The observed enhancement was ascribed to a *trans*-labilization effect of coordinated acetate on the Cr–C bond.

The anion acceleration of heterolysis for $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{CN}^{2+}$ by oxalate, hypophosphite, pyrophosphate, phosphate and oxalacetic acid has been studied in detail.⁴⁵

Conclusion. The organopentaaquachromium(III) complexes decompose by homolysis and heterolysis. The interest in these mechanisms arose as they serve as a model system for the behavior of metal-carbon σ bonds in aqueous solutions and as these complexes are relatively easily prepared. Using different anions to catalyse the reactions of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$, one can obtain the desired decomposition rate. Since $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes homolyse to free radical, it may be possible to use these chromium complexes as a free radical reservoir for radical reaction analogous to the coenzyme B₁₂ in biological systems.

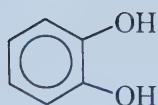
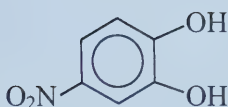
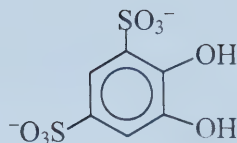
Chemistry of Fe(III) Catecholate Complexes

Iron is an essential element for microbial growth. Microorganisms synthesize iron(III)-specific chelating agents (siderophores) that can solubilize iron from the external environment by complexation, and transport it into the cell. One important siderophore is enterobactin, which is a microbial iron transport agent produced by bacteria such as *E. coli* and *S. typhimurium*.^{46,47} The enterobactin molecule is 3-fold symmetric and is comprised of three catecholate groups suspended from a trilactone backbone (see structure **VI**); metal coordination at neutral pH occurs through the six catecholate oxygens.



VI (H_6ent)

Unfortunately, studies of the coordination chemistry of enterobactin are difficult because of the extensive hydrolysis of the ester-linkage of the backbone ring in acidic and basic solution, and because the ferric complex appears to be oxidatively unstable in acidic medium.^{48,49} These problems have generated a number of studies of simpler models of enterobactin. These models involve simple catechol-containing ligands such as catechol (**VII**), 4-nitrocatechol (**VIII**) and Tiron (**IX**). Raymond and co-workers⁵⁰ determined the stability constants of the ferric complexes with these ligands in aqueous solutions in the pH range 2–11 by potentiometric and spectroscopic

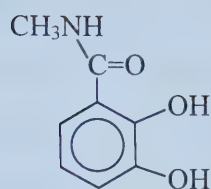
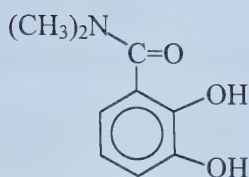
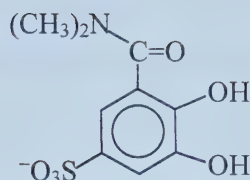
VII (H₂cat)VIII (H₂ncat)

IX

methods. The results indicated the presence of mono, bis, and tris complexes for Fe-cat, Fe-Tiron and Fe-ncat in the pH ranges (3.3–4.5, 6.0–7.0, >8.5), (<2.8, 4.1–5.2, >6.8) and (1.8–2.4, 3.5–4.2, >5.4), respectively. The results for Fe-Tiron were similar to those reported by McBryde.⁵¹ From the stability constants K_{FeL_3} ($[\text{FeL}_3^{3-}]/[\text{Fe}^{3+}][\text{L}^{2-}]^3$) of the tris-complexes, Raymond et al.⁵⁰ estimated that the stability constant of enterobactin with ferric ion is greater than 10^{45} M^{-1} .

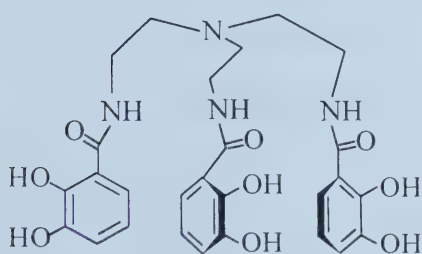
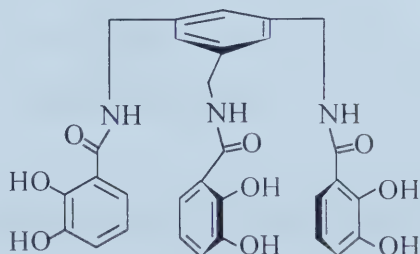
The crystal structure of $[\text{Fe}(\text{ent})]^{3-}$ has not been determined, but the structures of $[\text{Fe}(\text{cat})_3]^{3-}$, $[\text{V}^{\text{IV}}(\text{ent})]^{2-}$ and $[\text{Ga}(\text{cat})_3]^{3-}$ show that three catecholate groups lose six protons and coordinate to the metal ion, giving approximately C_3 molecular point symmetry.^{52–54} The conformational analysis by NMR of the diamagnetic Ga^{III} complex and molecular mechanics calculations on the $\text{Fe}(\text{III})$ complex of enterobactin have been reported.^{55,56}

In view of the structure of enterobactin, amide carbonyl oxygens on catechol rings may be potential chelating groups, therefore closely related model ligands containing an amide group such as *N*-ethyl-2,3-dihydroxybenzamide (H₂EBA), *N,N*-dimethyl-2,3-dihydroxybenzamide (H₂DMB), and *N,N*-dimethyl-2,3-dihydroxy-5-sulfo-benzamide (H₂DMBS) (see **X–XII**) were used to estimate the stability constant of $[\text{Fe}(\text{ent})]^{3-}$ complex and the value of 10^{52} M^{-1} was reported.⁴⁸ The experimental results showed that in neutral conditions, these catecholamide-containing ligands still

**X** (H₂EBA)**XI** (H₂DMB)**XII** (H₂DMBS)

employ the two hydroxyl groups to chelate Fe(III), in the same way as catechol.

Recently, more enterobactin-like ligands such as H₆TRENCAM (**XIII**), H₆MECAM (**XIV**) and H₆MECAMS (sulfo-H₆MECAM) were synthesized and studied.^{52,57–60} These enterobactin analogues are hydrolytically stable and are better models for enterobactin than catechol and H₂DMB because they have entirely secondary amide linkages like enterobactin. These Fe(III)-triscatecholamide complexes bind iron through the six phenolic oxygens of three 2,3-dihydroxybenzoyl groups and have a high affinity for ferric ion. Using these models, the value of 10⁴⁹ M⁻¹

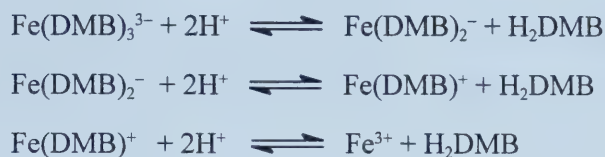
**XIII** (H₆TRENCAM)**XIV** (H₆MECAM)

for the stability constant of [Fe(ent)]³⁻ was estimated.⁵⁹

Although all the catecholate and tricatecholate ligands form the same type of complex at high pH, the protonation equilibria observed as the pH is decreased are

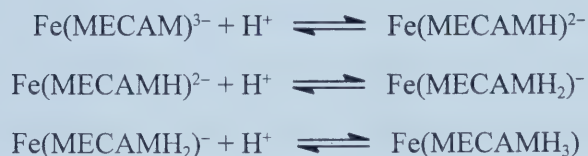
strongly dependent on the ligand structure. Bidentate catecholate ligands coordinate and dissociate as a unit and in the process either release or consume 2 equivalents of hydrogen ion. The protonation of FeL_3 ($\text{L}=\text{DMB}$ or catechol) by titration showed that the protonation of the tris-complexes proceeds in two-proton steps as shown in Scheme V.⁴⁸

Scheme V



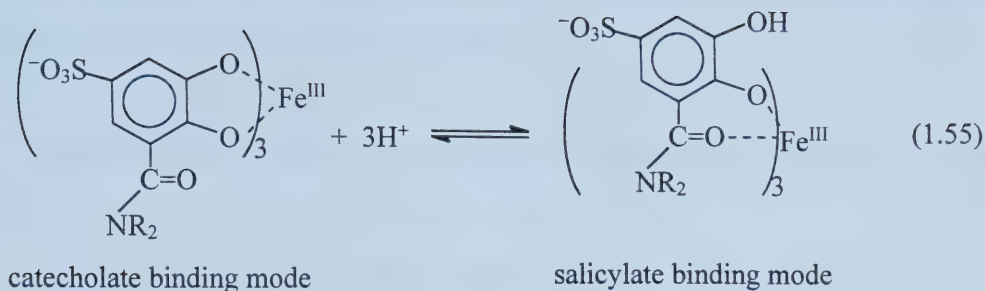
However, the titration results indicated that the tricatecholate complexes of $\text{Fe}(\text{MECAM})^{3-}$, $\text{Fe}(\text{MECAMS})^{3-}$ and $\text{Fe}(\text{TRENCAM})^{3-}$ are protonated in discrete one-proton steps as shown in Scheme VI.^{57,58}

Scheme VI

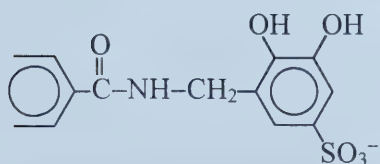


It has been shown by IR studies that the protonation of $\text{Fe}(\text{MECAMS})^{3-}$ and $\text{Fe}(\text{MECAM})^{3-}$ produces a shift from catecholate binding to salicylate binding as in eq 1.55.^{48,61}

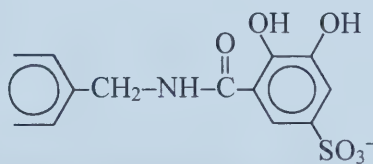
In order to support such a shift in the mode of bonding, the TRIMCAMS (**XV**) was synthesized. It is an isomer of MECAMS and the carbonyl groups in TRIMCAMS



are adjacent to the central benzene ring instead of α to the dihydroxybenzene rings (see the following structures).⁵⁸ This structural change makes the carbonyl groups in



XV (TRIMCAMS)



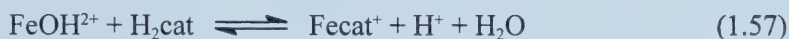
XVI (MECAMS)

TRIMCAMS unable to form a stable six-membered chelate ring with the *ortho* phenol and the protonation of the ferric complex of TRIMCAMS proceeds in two-proton steps. The results are explained by the double protonation like the simple catechol complexes and concomitant dissociation of one of the (dihydroxybenzyl)amide side groups. Thus one-proton reactions are predicted only when there is an α -carbonyl group *ortho* to one of the catecholate oxygens.⁵⁸ However, the ferric DMB system contradicts this prediction because it undergoes two-proton steps (Scheme V) and appears not to use the amide carbonyl oxygen. Raymond⁴⁸ suggested that, under the very dilute conditions (6×10^{-3} M), the DMB "salicylate" complex disproportionates

to the "catecholate" complex as shown in eq 1.56 and this disproportionation is unfavorable for the tricatecholate complexes.



Although there have been numerous studies of the stabilities of ferric complexes with catechol-containing ligands, there have been very few studies of the kinetics of the complex formation. The formation rates of mono ferric complexes of a series of simple catecholate ligands were studied in acidic media and the results are consistent with reaction 1.57 proceeding by an I_d mechanism.⁶²

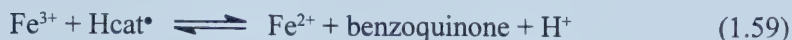


Ligand substituents have little effect on the formation rate constant ($\sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$), but they do affect the reverse reaction rate.

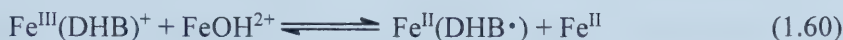
The formation kinetics of bis and tris complexes have not yet been studied apparently because the high pH required for complex formation will result in hydrolysis and polymerization of aqueous ferric ion. This problem could be overcome by studying the dissociation rate of the bis and tris complexes. Then the available equilibrium constants could be used to calculate the formation rate of bis and tris complexes, and the systems would be fully characterized kinetically.

Some catechol complexes with Fe(III) are unstable in acidic media due to the redox reaction between Fe(III) and catechols. The mechanism of the redox reaction is not fully understood. Earlier, Mentasti et al.⁶³ found that, at $\text{pH} < 2.0$, iron(II) is produced and catechol is converted to benzoquinone. The mechanism suggested

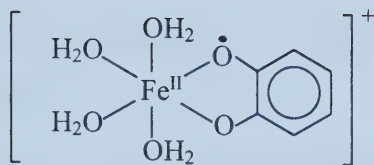
involved formation of the intermediate semiquinone radical ($\text{Hcat}^\bullet$) as the rate-controlling step; $\text{Hcat}^\bullet$ was then oxidized to benzoquinone, according to eq 1.58–1.59.



The kinetics of oxidation of 2,3-dihydroxybenzoic acid (DHB) by Fe(III) in acidic conditions has been studied by Jordan and Xu.⁶⁴ The mechanism (eq 1.60–1.62) is different from eq 1.58–1.59. The Fe(III)-DHB complex does not simply undergo intramolecular electron transfer, and the more labile FeOH^{2+} is involved in the first step in eq 1.60.

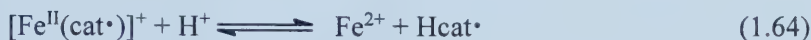


Qualitative examination of electron spin resonance spectra indicated the oxidation of catechol by ferric ion, at pH values as high as 4, produced at least some semiquinone radical.⁵⁰ However, Silver and co-workers⁶⁵ reported that no benzoquinone was produced and the 1:1 iron-catechol complex was stable over the pH range 2.8–4.5. From Mössbauer data, they suggested that the complex is an Fe(II) species and proposed a formulation in which the deprotonated catechol radical is chelated with Fe(II) as shown in structure **XVII**. In order to explain the fast redox reaction in $\text{pH} < 2$ reported by Mentasti et al.,⁶³ Silver and co-workers⁶⁵ suggested that



Structure XVII

below pH 2.0 the stable complex $[\text{Fe}^{\text{II}}(\text{cat}^\bullet)]^+$ decomposes to Fe(II) and semiquinone due to protonation of the complex as shown in eq 1.63–1.65.



The observation of the semiquinone in the ESR at pH 4 would be explained by the equilibrium $[\text{Fe}^{\text{II}}(\text{cat}^\bullet)]^+ \rightleftharpoons \text{Fe}^{2+} + \text{cat}^\bullet$, or by eq 1.65.

Raymond et al.⁵⁰ suggested that the redox reaction occurs in the mono-complex and the ferric state is completely stabilized against reduction by the catechol only with the formation of at least the bis-complex. Since the more acidic catechols begin to coordinate ferric ions at lower values of pH, their stability to ferric ion oxidation extends to lower values of pH. The ease with which the catechol ligand can reduce ferric ions in acidic solutions depends also on the base strength of the catechol, since this is a function of both the oxidation potential of the catechol and its ferric ion affinity. This predicts that the Fe(III) complexes of the catechol ligands with electron-withdrawing substituents should be more stable in acidic conditions, compared with those ligands having electron-donating substituents. In agreement with this prediction, Mentasti et al.⁶⁶ found that the Fe(III) complexes of 4-COOH-, 4-CN- catechol

complexes are stable in acidic solution, while 4-methyl- and 4-*t*-butyl- catechol complexes undergo a redox decomposition.

In conclusion, a number of catechol-containing ligands have been studied as models for enterobactin, and most of the work has focused on the thermodynamic measurements. The stability constant of enterobactin was estimated from the models as $>10^{45} \text{ M}^{-1}$. Enterobactin is an excellent iron transport ligand due to its high affinity for ferric ion. The mechanism of the redox reaction and chelate formation of Fe(III) complexes with the catechol-containing ligands in acidic medium is still not fully understood.

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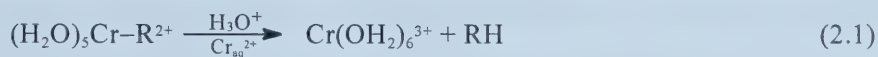
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Chapter 2. Kinetics of Heterolysis of Pentaquachromium(III) Complexes of Benzyl and 4-Methyl-, Cyano-, and Fluoro-Substituted Benzyl Ligands*

Introduction

Pentaquachromium(III) forms a wide range of organometallic derivatives¹ of the general formula $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ that decompose in aqueous solution by heterolysis (eq 2.1) and homolysis (eq 2.2). The addition of aqueous chromium(II), as done in this



study, suppresses the initial homolysis equilibrium in eq 2.2, and allows the heterolysis reaction to be studied. Homolysis is promoted by the addition of scavengers for chromium(II) and/or $\text{R}\cdot$, and this reaction will be discussed in Chapter 3.

The decomposition of the benzyl complex, $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$, was studied initially by Kochi and Buchanan² and later by Nohr and Espenson³ who found much lower heterolytic reactivity than reported previously. More recent work⁴ has established the heterolytic and homolytic reactivity of the benzyl complex.

The present study involves an examination of the effect of substituents on the benzene ring on the heterolytic reactivity of the benzyl derivatives. Nohr and

* A version of this chapter has been published. Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1993**, 32, 5472–5476.

Espenson³ studied the homolysis of the 4-CH₃, 4-Br, 4-CF₃ and 4-CN derivatives and found that homolysis is slower with more electron withdrawing substituents, with a good correlation of the rate constant and Hammett σ parameter. However, there is no information on the substituent effects on heterolysis. It is also found here that the 4-CN system is more complex than reported by Nohr and Espenson because it undergoes a protolytic equilibrium.

Results

The benzyl derivatives of (H₂O)₅Cr-R²⁺ were prepared by reaction of the appropriate benzyl bromide with chromium(II) perchlorate in 40:20 by volume methanol:water solution, and were isolated by ion exchange chromatography at 0 °C in 1.0 M NaClO₄ containing 0.01 M HClO₄. The electronic spectra data of the (H₂O)₅Cr-R²⁺ complexes are given in Table 2.1. The results are in agreement with earlier observations of Kochi and Davis⁵ on similar systems. It should be noted that these complexes have a longer wavelength, weak absorption⁴ at ~530 nm which has not been characterized here.

Below 400 nm, the longest wavelength maximum shifts to lower wavelength with increasing electron withdrawing power of the substituents on the benzene ring. For the cyano-substituted derivatives this maximum is at 316-318 nm, while for the other derivatives it is between 348 and 362 nm. The high molar extinction coefficients and peak position trends indicate that these bands may be due to ligand to metal charge transfer. The typical electronic spectra of benzyl and 2,4-difluoro complexes in aqueous 0.10 M HClO₄ are shown in Figure 2.1. For the cyano-substituted derivatives, some peaks overlap and a Gaussian shape has been assumed to fit and resolve the experimental spectra. For example, four peaks at 316, 292, 259 and 224 nm in Figure

Table 2.1. Electronic Spectra of (H₂O)₅Cr–R²⁺ Complexes^a

R	$\lambda_{\max}$, nm ($10^{-3} \times \epsilon$, M ⁻¹ cm ⁻¹)			
4-CH ₃ C ₆ H ₄ CH ₂	362(2.16)	304(7.25)		
C ₆ H ₅ CH ₂	356(2.25)	296(6.97)	274(7.67)	242(9.45)
4-FC ₆ H ₄ CH ₂	354(2.10)	292(6.60)	272(8.07)	238(6.17)
2,4-F ₂ C ₆ H ₃ CH ₂	350(2.155)	294(6.85)	270(7.91)	236(6.80)
3,5-F ₂ C ₆ H ₃ CH ₂	348(2.25)	294(7.62)	274(7.53)	240(5.91)
2-NCC ₆ H ₄ CH ₂	316(6.57) ^b	282(8.51) ^b		230(9.88)
3-NCC ₆ H ₄ CH ₂	318(4.56) ^c	282(9.36) ^c		232(11.27)
4-NCC ₆ H ₄ CH ₂	316(7.42) ^d	292(5.33) ^d	259(4.61) ^d	224(6.05) ^d

^a Spectra recorded in aqueous 0.10 M HClO₄/0.90 M NaClO₄. ^b From fitting the experimental spectrum with peaks at 316 nm (ϵ 6.57 $\times 10^3$) and 282 nm (ϵ 8.51 $\times 10^3$) to two Gaussian curves to obtain the positions and ϵ 's tabulated. ^c From fitting the experimental spectrum with peaks at 284 nm (ϵ 9.76 $\times 10^3$) and $\sim$ 315 nm (ϵ 5.0 $\times 10^3$) to two Gaussian curves to obtain the positions and ϵ 's tabulated. ^d From fitting the experimental spectrum with peaks at 310 nm (ϵ 9.18 $\times 10^3$), 264 nm (ϵ 5.31 $\times 10^3$) and 224 nm (ϵ 6.05 $\times 10^3$) to four Gaussian curves to obtain the positions and ϵ 's tabulated (see Figure 2.2).

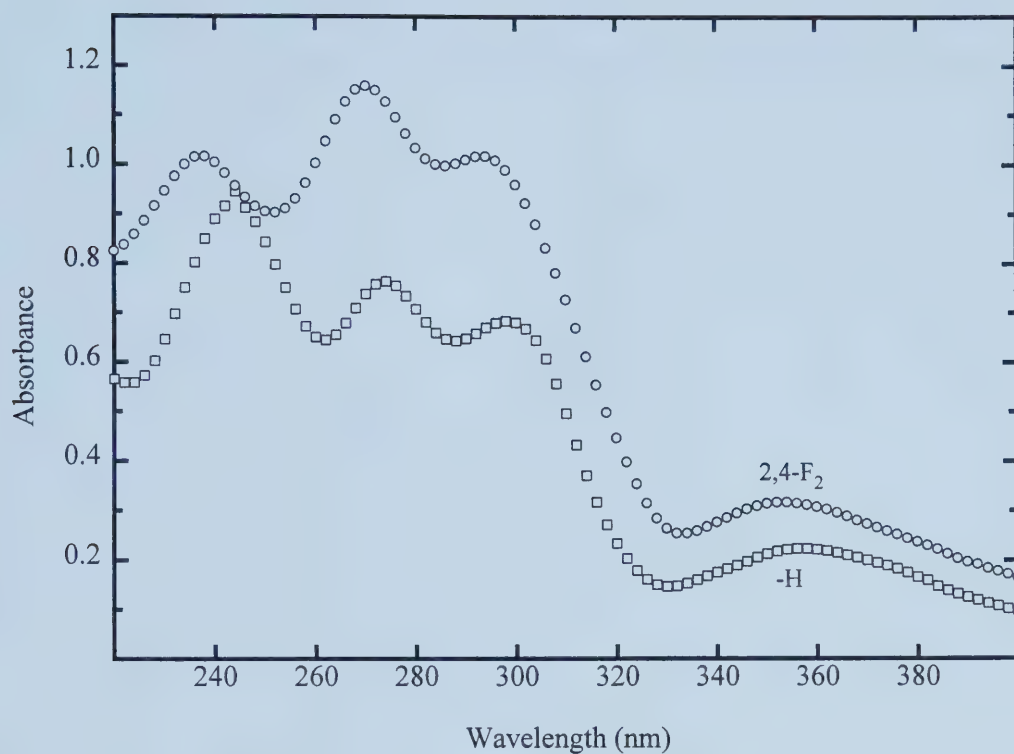


Figure 2.1. Spectra of the benzyl (2.02×10^{-5} M) and 2,4-difluorobenzyl (2.96×10^{-5} M) complexes of pentaquachromium(III) with a 50 mm path length and in aqueous 0.10 M HClO_4 /0.9 M NaClO_4 .

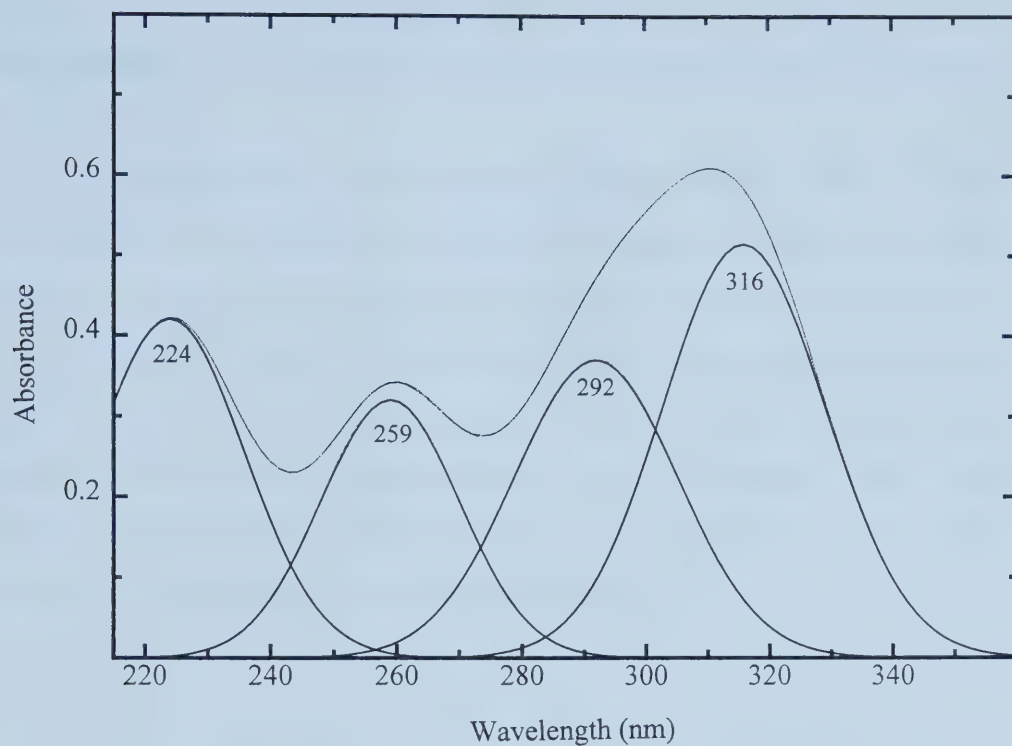
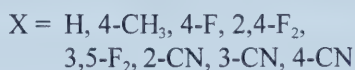
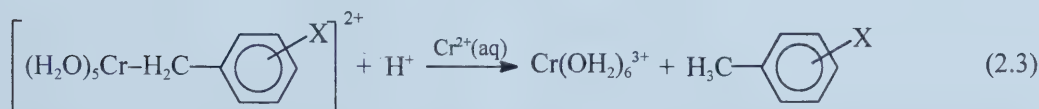


Figure 2.2. Electronic spectrum of 4-cyanopentaaquabenzylchromium(III) complex (1.40×10^{-5} M) and four Gaussian curves resolved from the experimental spectrum with a 50 mm path length and in aqueous 0.10 M HClO_4 /0.9 M NaClO_4 .

2.2 are resolved from the experimental spectrum of the 4-cyano substituted derivative. The wavelengths of maximum absorbance are unaffected by changing the acidity from 0.01 to 1.00 M.

The organic products of the heterolysis were identified by ^1H NMR in CDCl_3 , after extraction into chloroform and evaporation of the organic extract. The reactant solutions contained $(1.8\text{--}3.2) \times 10^{-3}$ M $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ (0.12–0.20 mmol) and 0.04 M Cr(II) in 0.10 M HClO_4 . The product was 100% of the corresponding toluene derivative, except for $\leq 4\%$ aldehyde with benzyl and $\leq 10\%$ bibenzyl with the 3-cyano complex. The latter minor products probably arise from reaction with O_2 and spontaneous homolysis, respectively, and may be contaminants in the starting solution. Therefore the reaction being observed is described by eq 2.3.



The heterolysis kinetics for each complex were determined from the decrease in absorbance of the peak or shoulder in the 310–362 nm region. The rate was studied as a function of $[\text{H}^+]$ and temperature. All of the systems, except the 2- and 4-cyano complexes, show a common pattern for the variation of rate constant with $[\text{H}^+]$, and typical results for the 2,4-difluoro and benzyl systems are shown in Figure 2.3. From past experience,¹ one expects the heterolysis rate constant to be composed of two terms, one independent of and one first order in $[\text{H}^+]$, e.g. $k_{\text{het}} = k_0 + k_1[\text{H}^+]$ (see eq 1.32 in Chapter 1) and the plot of k_{het} vs. $[\text{H}^+]$ should be linear. The representative

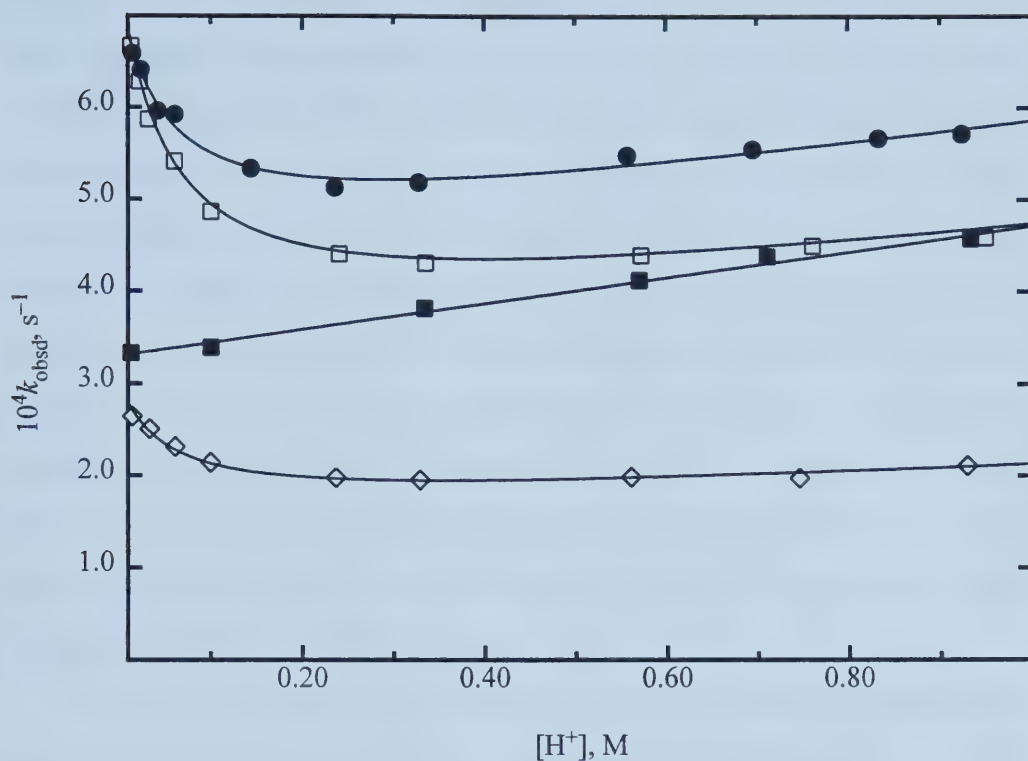
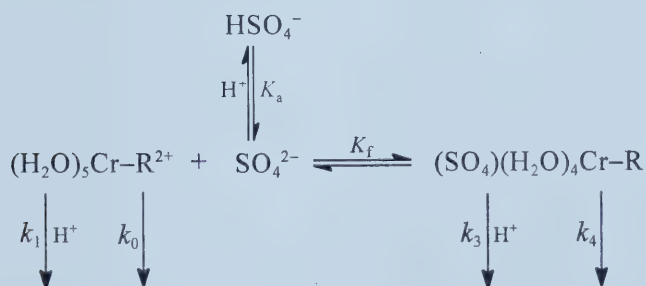


Figure 2.3. Dependence of the heterolysis rate on hydrogen ion concentration for $(\text{H}_2\text{O})_5\text{-Cr(III)}$ complexes of 2,4-difluorobenzyl ($\square$ 74.0 °C, 0.0247 M chromium(II) sulfate; $\diamond$ 64.0 °C, 0.0414 M chromium(II) sulfate) and benzyl ($\bullet$ 67.3 °C, 0.0426 M chromium(II) sulfate; $\blacksquare$ 67.3 °C, 0.0426 M chromium(II) perchlorate).

results in Figure 2.3 correspond to this expectation only for $[H^+] > 0.2$ M. In the lower acidity region, the rate constant appears to have an $[H^+]^{-1}$ dependence. To make a long story short, this appearance is deceptive, and the rate is actually varying with sulfate ion concentration. For reasons of convenience and economy, many runs were done using chromium(II) prepared by zinc amalgam reduction of chromium(III) sulfate solutions. If sulfate is replaced by perchlorate as the source of Cr(II), the $[H^+]^{-1}$ dependence disappears, as shown for the benzyl complex in Figure 2.3. In Figure 2.4 and Figure 2.5, at fixed $[H^+]$, the rate constant appears to depend on the chromium(II) concentration, but this is due to sulfate catalysis, as shown by experiments with the benzyl complex, in which chromium(II) perchlorate was used, and in which zinc and sodium sulfate were added. The increase in rate at low $[H^+]$ is largely due to acid dissociation of HSO_4^- to yield SO_4^{2-} .

Except for the more reactive 2-cyano and 4-cyano complexes, the heterolysis is described by the reactions in Scheme I. Rapid pre-equilibrium formation of a sulfato

Scheme I



complex is based on previous work, which has shown that one H_2O ligand is rapidly replaced in $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ systems, even at 25 °C, by a variety of anions including thiocyanate,⁶ carboxylates⁷ and phosphates.⁸ In Scheme I, the k_3 step is formulated as

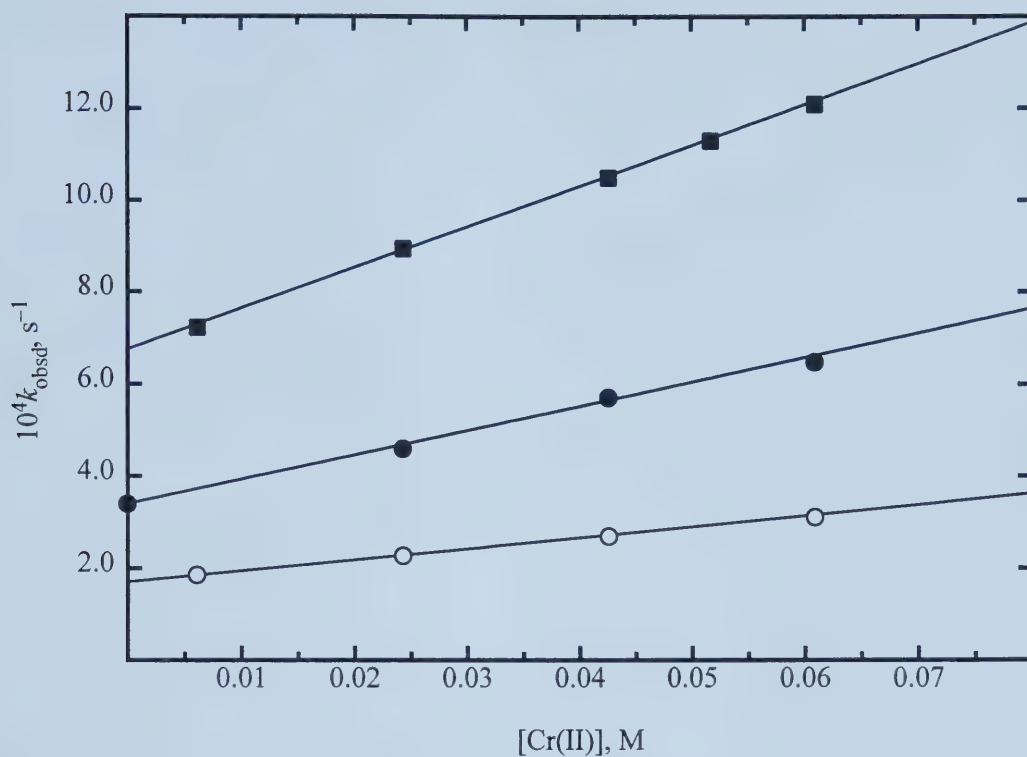


Figure 2.4. Dependence of the heterolysis rate on chromium(II) sulfate concentration for benzyl complex of pentaquachromium(III) (○ 59.3 °C, 0.100 M H^+ ; ● 67.3 °C, 0.100 M H^+ ; ■ 74.3 °C, 0.100 M H^+).

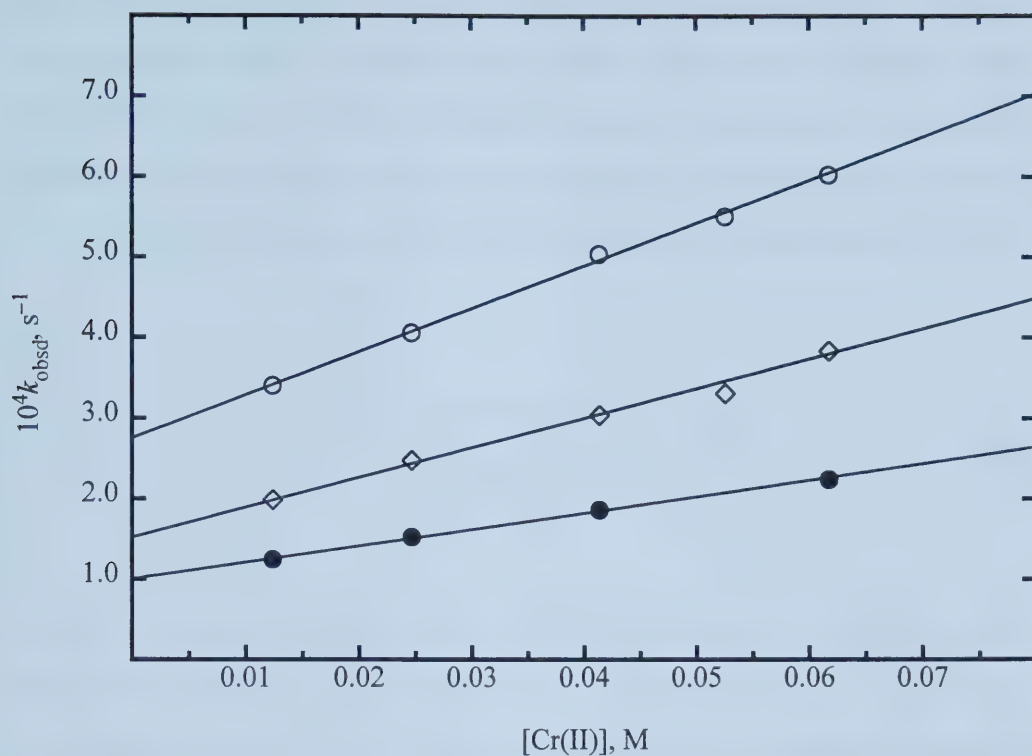


Figure 2.5. Dependence of the heterolysis rate on chromium(II) sulfate concentration for 3-cyanobenzyl complex of pentaquachromium(III) (● 64.0 °C, 0.100 M H^+ ; ◇ 69.0 °C, 0.100 M H^+ ; ○ 74.0 °C, 0.100 M H^+).

acid catalysed heterolysis of the sulfato complex, but it could equally be reaction of free or complexed HSO_4^- . These alternatives will be analysed in the Discussion section below. From Scheme I, with the assumption that K_a and K_f describe rapidly maintained equilibria, the predicted pseudo-first order rate constant is given by eq 2.4 (derivation of eq 2.4 is shown in Appendix 2.9), where the total sulfate concentration $[\text{SO}_4^{2-}]_t \gg$

$$k_{\text{obsd}} = \frac{(k_1[\text{H}^+] + k_0) + (k_3K_fK_a[\text{H}^+] + k_4K_fK_a)\left(\frac{[\text{SO}_4^{2-}]_t}{K_a + [\text{H}^+]}\right)}{1 + \left(\frac{K_fK_a[\text{SO}_4^{2-}]_t}{K_a + [\text{H}^+]}\right)} \quad (2.4)$$

$[\text{Cr(III)}]$. To analyse the data with eq 2.4, the K_a values have been interpolated from the results of Dickson et al.⁹ in aqueous NaCl solutions. For most experiments, it should be noted that $[\text{SO}_4^{2-}]_t$ is 1.5 times the chromium(II) concentration, because the chromium is derived from chromium(III) sulfate $\text{Cr}_2(\text{SO}_4)_3$. In all cases, the free H^+ concentration has been calculated after taking into account the H^+ bound to HSO_4^- .

Least-squares analysis of the k_{obsd} values to eq 2.4 indicates that $K_fK_a[\text{SO}_4^{2-}]_t/(K_a + [\text{H}^+]) < 1$, so that K_f cannot be evaluated from the data. The quality of the least-squares fits indicates an upper limit of $K_f < 10$. Therefore, only the composite values k_3K_f and k_4K_f can be evaluated and the data were fitted assuming $K_f = 1$. The temperature dependence of the rate constants or composites in eq 2.4 were represented by the transition state equation with activation parameters ΔH^* and ΔS^* , and the k_{obsd} values at three temperatures were fitted by least-squares to determine the activation parameters. The values are given in Table 2.2, and the complete data set and calculated and experimental k_{obsd} values are given in Appendixes 2.1–2.8. Reactivity trends are assessed in the Discussion section, but it should be noted that the activation

Table 2.2. Activation Parameters^a for the Heterolysis of Substituted Benzyl Complexes of Pentaquachromium(III)

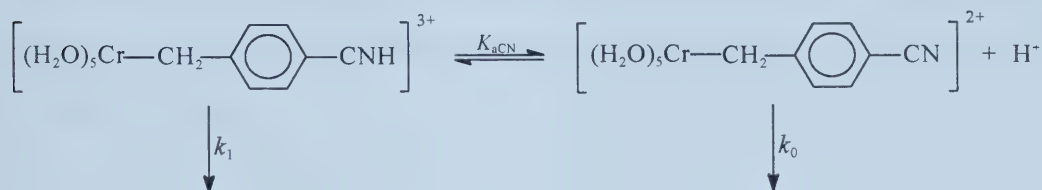
Substituent	k_1		k_0		k_3K_f		k_4K_f	
	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*
4-CH ₃	12.6±3	-39.5±9.2	19.1±0.4	-18.0±1	24.3±2	7.4±7	23.6±0.8	-0.6±3
H	8.6±3	-51.6±8	21.7±0.4	-11.0±1	20.8±2	-3.0±6	22.0±0.8	-4.3±2
4-F	17.1±3	-26.7±8	20.8±0.4	-13.6±1	23.3±3	4.2±9	27.5±1	9.6±4
2,4-F ₂	7.5±11	-57.3±31	22.9±0.9	-8.5±3	18.0±6	-13.0±18	25.1±1	9.6±4
3,5-F ₂	10.7±3	-46.0±9	21.4±1	-13.9±3	35.9±3	40.3±8	27.5±1	10.7±3
3-CN	13.9±5	-37.6±15	23.0±1	-8.9±3	24.4±3	6.6±8	24.6±1	7.6±4

^a Values of ΔH^* (kcal mol⁻¹) and ΔS^* (cal mol⁻¹ K⁻¹) obtained from least squares fits of data at three temperatures to eq 2.4; error limits are one standard deviation.

parameters for k_1 and k_3K_a are less well defined than those for k_0 and k_4K_a because the former make rather minor contributions. This can be seen for k_1 in Figure 2.3 where the increase in k_{obsd} for $[\text{H}^+] \geq 0.2 \text{ M}$ is distinct for the benzyl complex, but marginal for the 2,4-F₂ complex.

The 2-CN and 4-CN complexes differ from the others in that there is no apparent effect of sulfate ion and the $[\text{H}^+]$ dependence of k_{obsd} is different. The $[\text{H}^+]$ dependence for the 4-CN system is shown in Figure 2.6 and the saturation effect on k_{obsd} indicates a protonation equilibrium for the complex. Since this was not observed with the other substituents, the protonation appears to involve the 4-CN substituent and the system may be described by Scheme II which predicts that k_{obsd} is given by eq 2.5. Least-squares analysis gives the kinetic parameters in Table 2.3 for the 4-cyano complex. The full data set is given in Appendix 2.7.

Scheme II



$$k_{\text{obsd}} = \frac{k_1[\text{H}^+] + K_{\text{aCN}}k_0}{K_{\text{aCN}} + [\text{H}^+]} \quad (2.5)$$

For the 2-cyano complex, the k_{obsd} increases linearly with $[\text{H}^+]$, with no apparent saturation effect, as shown in Figure 2.7. This is the hydrogen ion dependence observed for many other such organochromium(III) complexes.¹ The

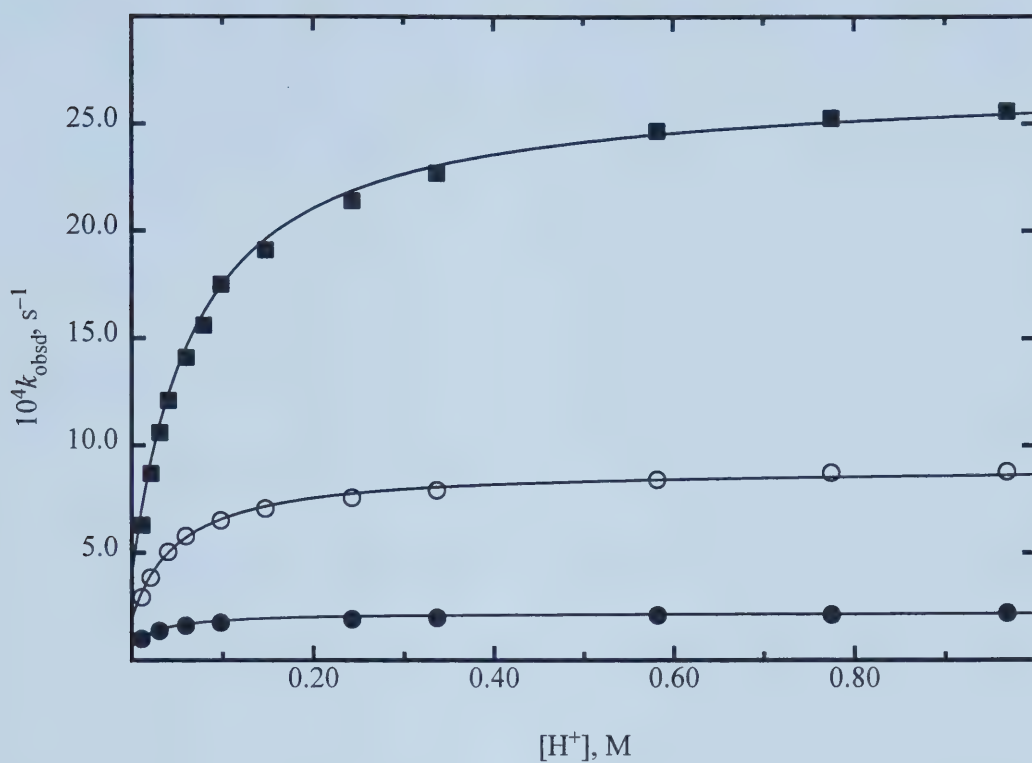


Figure 2.6. Dependence of the rate constant for heterolysis of the 4-cyanobenzyl complex of pentaquachromium(III) on hydrogen ion concentration at 25.0 (●), 35.0 (○) and 43.0 °C (■).

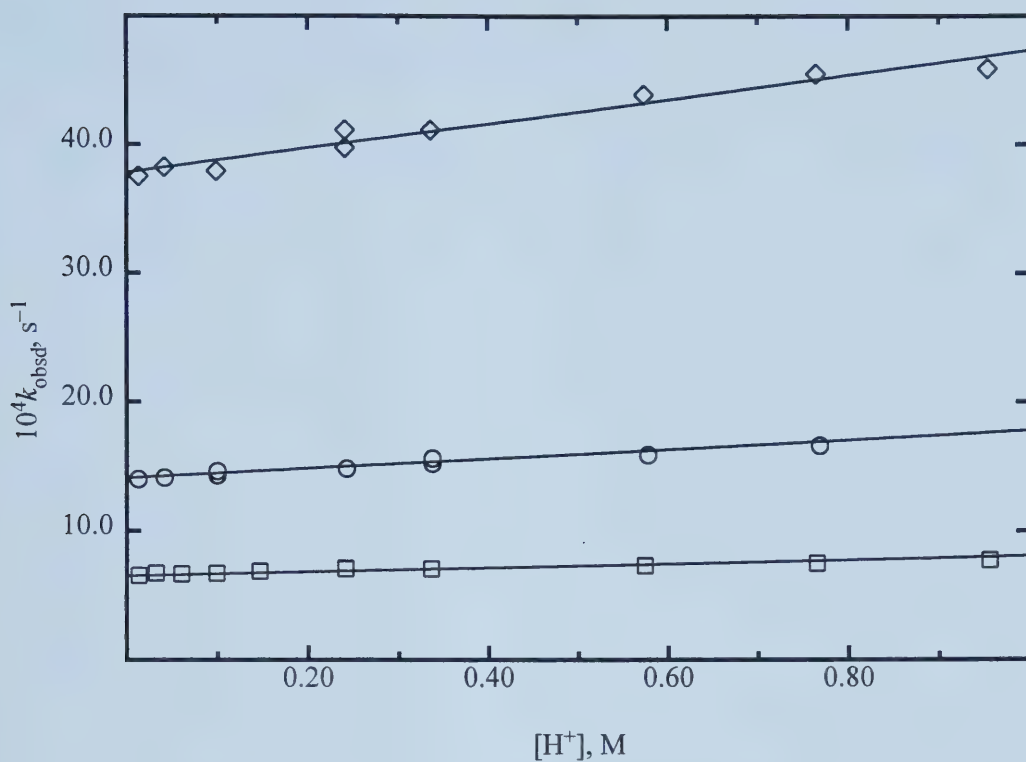


Figure 2.7. Dependence of the rate constant for heterolysis of the 2-cyanobenzyl complex of pentaquachromium(III) on hydrogen ion concentration at 57.0 ($\square$), 64.0 ($\circ$) and 74.0 °C ($\diamond$).

Table 2.3. Kinetic Parameters for the Heterolysis of the 4-Cyanobenzyl and 2-Cyanobenzyl Complexes of Pentaquachromium(III)^a

Parameter	4-cyanobenzyl	Parameter	2-cyanobenzyl
$k_1, \text{s}^{-1} (25\text{ }^\circ\text{C})$	1.95×10^{-4}	$k_1', \text{M}^{-1} \text{s}^{-1} (65\text{ }^\circ\text{C})$	3.3×10^{-4}
$\Delta H_1^*, \text{kcal mol}^{-1}$	25.5 ± 0.04	$\Delta H_1'^*, \text{kcal mol}^{-1}$	26.1 ± 0.5
$\Delta S_1^*, \text{cal mol}^{-1} \text{K}^{-1}$	10.3 ± 0.3	$\Delta S_1'^*, \text{cal mol}^{-1} \text{K}^{-1}$	2.5 ± 2.7
$k_0, \text{s}^{-1} (25\text{ }^\circ\text{C})$	6.4×10^{-5}	$k_0, \text{s}^{-1} (65\text{ }^\circ\text{C})$	1.6×10^{-3}
$\Delta H_0^*, \text{kcal mol}^{-1}$	16.5 ± 0.5	$\Delta H_0^*, \text{kcal mol}^{-1}$	22.7 ± 0.06
$\Delta S_0^*, \text{cal mol}^{-1} \text{K}^{-1}$	-22.5 ± 1.9	$\Delta S_0^*, \text{cal mol}^{-1} \text{K}^{-1}$	-4.6 ± 0.3
$K_{\text{aCN}}, \text{M} (25\text{ }^\circ\text{C})$	3.15×10^{-2}		
$\Delta H_{\text{aCN}}^\circ, \text{kcal mol}^{-1}$	6.14 ± 1.4		
$\Delta S_{\text{aCN}}^\circ, \text{cal mol}^{-1} \text{K}^{-1}$	13.7 ± 4.4		

^a Values of ΔH^* , ΔS^* , ΔH° and ΔS° obtained from least-squares fits of data at three temperatures: error limits are on standard deviation.

standard interpretation would be that the reaction proceeds by parallel pathways involving attack by hydrogen ion (k_1') and water (k_0), respectively, so that k_{obsd} is given by eq 2.6. However, the experience with the 4-cyano complex raises the possibility that the 2-cyano system also might be described by Scheme II and eq 2.5, with the modification that $K_{\text{aCN}} > [\text{H}^+]$, so that no saturation is observed. The K_{aCN} might be

$$k_{\text{obsd}} = k_1'[\text{H}^+] + k_0 \quad (2.6)$$

increased by the proximity of the Cr(III) in the 2-cyano complex compared the 4-cyano complex. Then k_1' equals k_1/K_{aCN} in terms of the parameters in Scheme II. A possible selection between these alternatives will be discussed in the light of overall reactivity trends. The kinetic parameters are summarized in Table 2.3, and the full data set is given in Appendix 2.8.

Discussion

From the rate constants given in Table 2.4, it can be seen that there is a general trend to decreasing reactivity with increasing electron withdrawing power of the substituent based on the Hammett σ values.¹⁰ The values of k_0 show a correlation with the Hammett σ parameter ($\log k_0 = -3.53 - 0.63\sigma$) except for the 2-CN and 4-CN systems, as illustrated in Figure 2.8. The latter are much more reactive than expected from their σ values. Aside from these two exceptions, the rate constant changes by less than 10-fold with substituent.

All of the systems studied here show a well defined uncatalysed heterolysis pathway (k_0) with activation parameters that fall in a narrow range of 21 ± 2 for ΔH_0^*

Table 2.4. Summary of Rate Constants for the Heterolysis of Substituted Benzyl Complexes of Pentaquachromium(III)

substituent	$10^5 k_1, \text{M}^{-1} \text{s}^{-1}$		$10^5 k_0, \text{s}^{-1}$		$10^3 k_3 K_f, \text{M}^{-2} \text{s}^{-1}$		$10^4 k_4 K_f, \text{M}^{-1} \text{s}^{-1}$		σ^a
	25.0	65.0 °C	25.0	65.0 °C	25.0	65.0 °C	25.0	65.0 °C	
4-CH ₃ ^b	0.77	11	0.69	36	0.41	59	0.47	58	-0.14
H ^b	1.7	11	0.33	28	0.82	59	0.56	51	0.0
4-F ^b	0.25	8.5	0.39	28	0.45	53	0.22	61	0.06
2,4-F ₂ ^b	0.62	3.1	0.14	15	0.58	24	0.12	29	0.60
3-CN ^b	0.25	4.5	0.097	11	0.24	35	0.12	26	0.62
3,5-F ₂ ^b	0.77	7.4	0.12	9.9	0.019	28	0.09	25	0.68
4-CN ^c	20	4000	6.4	190					0.70
2-CN ^c		0.16	33	1.5	160				
1.06									

^a Hammett substituent constant. ^b Values at 25 °C obtained by extrapolation using activation parametrs in Table 2.2. ^c Values 65 °C obtained by extrapolation using activation parameters in Table 2.3.

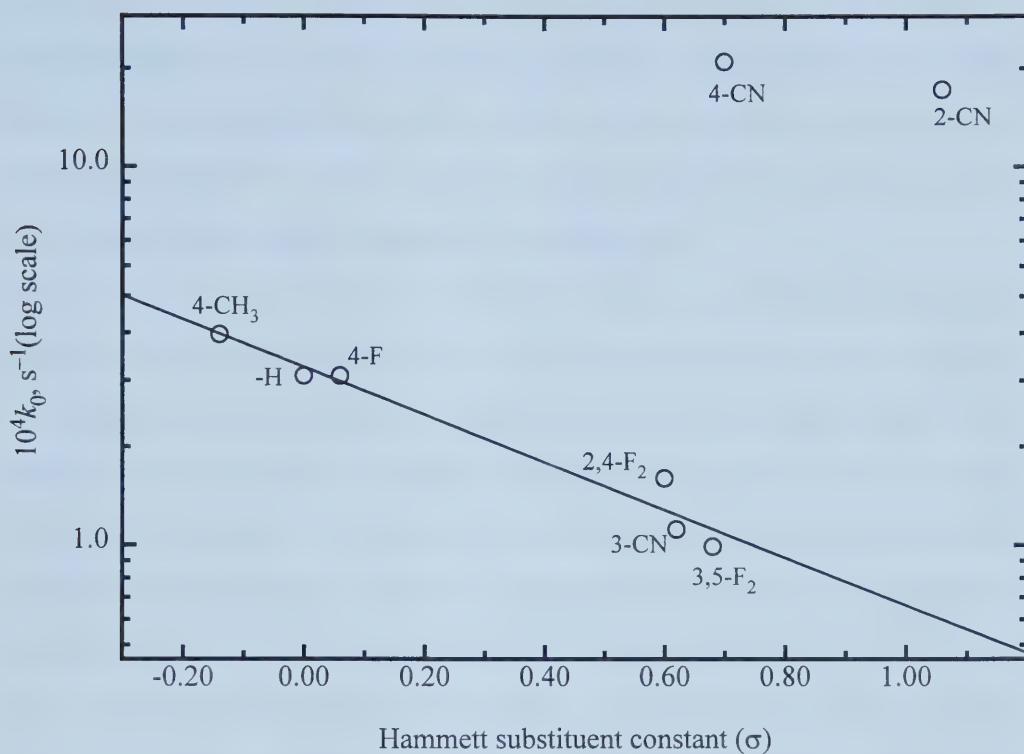


Figure 2.8. A plot illustrating the LFER correlation of k_0 (65°C) with the Hammett σ substituent constant; $\log k_0 = -3.53 - 0.63 \sigma$ ($r = 0.98$). Values for 4-CN and 2-CN obtained by extrapolation from 25°C have an uncertainty of $\pm 4 \times 10^{-4}$ and $\pm 1 \times 10^{-4} \text{ s}^{-1}$, respectively.

and -13.5 ± 5 for ΔS_0^* , except for the 2-CN and 4-CN complexes. These parameters are similar to those for a number of Cr-CH₂X systems,¹ where it is also observed that electron withdrawing -X groups reduce k_0 . This can be understood generally in terms of reduced susceptibility of the -CH₂ to electrophilic attack, in the absence of steric and hydrogen bonding complications of the organic group.

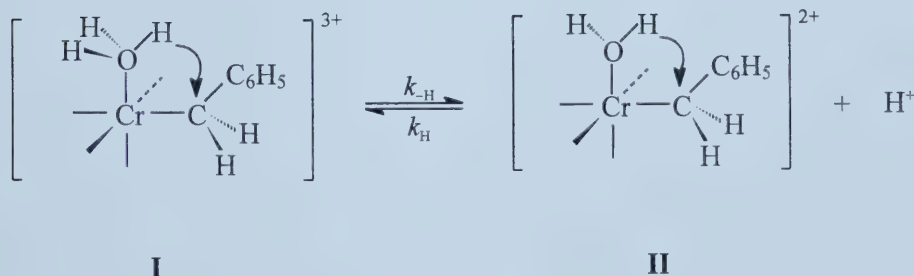
The k_0 values for the 2-CN and 4-CN systems are $>10^2$ times larger than expected from the σ correlation. For the 4-CN complex, the larger k_0 may be attributed to conjugative delocalization of the negative charge of the -CH₂ group which should weaken the Cr-C bond. This is consistent with the lower ΔH_0^* and the observation that this ligand undergoes protonation. This effect seems to dominate over the less favorable electrophilic attack on the -CH₂. The conjugative effect also can operate for the 2-CN complex, but proton saturation is not observed, and the ΔH_0^* value is in the normal range. The high reactivity of the 2-CN complex is due to a more favorable ΔS_0^* which seems more indicative of steric acceleration. The failure to detect proton saturation shows that the 2-cyanobenzyl ligand is less basic than the 4-cyano analogue. Protonation might be less favored because of hydrogen bonding of the 2-CN substituent with *cis*-H₂O ligands. Steric interactions of these same groups may inhibit conjugation by making it more difficult for the -CH₂ carbon to approach the sp² hybridization required for optimum conjugation.

The acid catalysed pathway (k_1) makes a minor contribution for many of these systems, as can be seen from the small slopes at higher acidities in Figure 2.3, and the larger uncertainties on ΔH_1^* and ΔS_1^* in Table 2.2. Some of this contribution could be due to medium effects of replacing Na⁺ by H⁺ to maintain ionic strength, but this cannot be the whole effect because it does vary with the benzyl substituent. In addition, the lower ΔH_1^* than ΔH_0^* and large negative ΔS_1^* values are typical of results on other systems where this is a dominant term.¹

It is interesting to note that the activation parameters for k_1 show a good isokinetic relationship ($\Delta H_1^* = 25.2 + 0.31\Delta S_1^*$) as shown in Figure 2.9. The relationship also fits the k_1' parameters for the 2-CN complex (not shown in Figure 2.9). However, neither k_1 nor k_1/K_{aCN} for the 4-CN system fits this correlation. If the isokinetic relationship implies a commonality of mechanism, then it appears that the 2-CN ligand reacts by the normal acid catalysed process rather than pre-equilibrium ligand protonation.

It is not certain how the H^+ catalysis operates in normal systems of this type. The simplest possibility is electrophilic attack of H_3O^+ on the $-\text{CH}_2$ group, but Espenson and co-workers¹¹ found that the hydrolytic reactivity is profoundly reduced if the *cis*-water ligands in such complexes are replaced by an N_4 -macrocycle. These observations are not consistent with direct electrophilic attack, and suggest involvement of the *cis*-water ligands in the heterolytic cleavage. The heterolysis might proceed as indicated in Scheme III by structures **I** and **II** for k_1 and k_0 , respectively.

Scheme III



Structure **I** involves H^+ transfer from a protonated coordinated water ligand. There is some precedent for such species from observations¹³ that similar aquachromium(III)

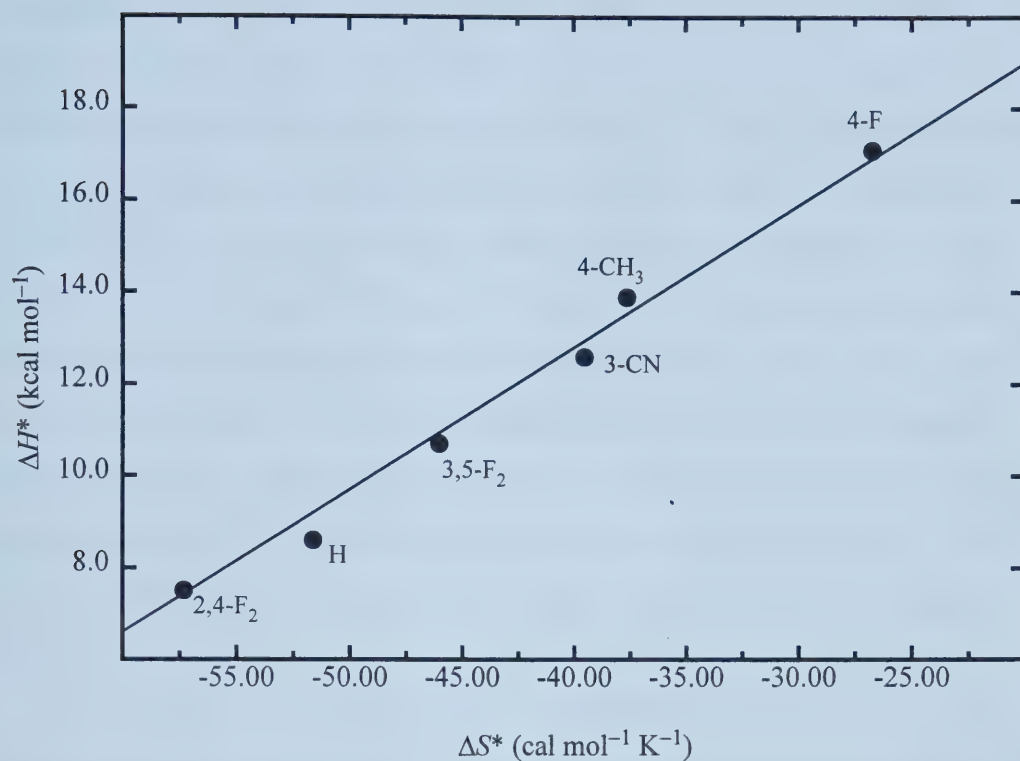


Figure 2.9. The isokinetic relationship between $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ ($\Delta H_1^\ddagger = 25.2 + 0.31 \Delta S_1^\ddagger$).

complexes undergo proton exchange with solvent water by an H^+ catalysed path. For $(H_2O)_5CrCH_2CN^{2+}$, the $k_H = 6.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C), and if one assumes that the proton dissociation is diffusion controlled, with $k_{-H} \approx 1 \times 10^{10} \text{ s}^{-1}$, then the acid dissociation constant ($K_{aM} = k_{-H}/k_H$) of **I** is $\sim 1.6 \times 10^5 \text{ M}$. The activation energy for k_H (3.7 kcal mol⁻¹) and a typical diffusion activation energy for k_{-H} gives $\Delta H_{aM}^\circ \approx -2 \text{ kcal mol}^{-1}$, and one can estimate that $\Delta S_{aM}^\circ \approx 17 \text{ cal mol}^{-1} \text{ K}^{-1}$. If **I** is the reactive species for the acid catalysed heterolysis, then the experimental k_1 values are really k_1''/K_{aM} and k_1'' will be in the range of $0.4\text{--}3 \text{ s}^{-1}$ (25 °C) for the systems here, and have a ΔS^* about $17 \text{ cal mol}^{-1} \text{ K}^{-1}$ more positive than the experimental values for k_1 . The latter change places the ΔS^* for k_1'' in the same range as those for k_0 , and the result that $k_1'' \gg k_0$ is consistent with the expected greater electrophilicity of coordinated H_3O^+ compared to H_2O .

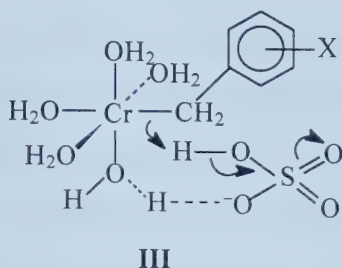
The 4-CN complex is expected to be different because the unique saturation effect with $[H^+]$ implies a quite different type of protonation. The protonation described in Scheme II is analogous to that found¹² for the acetamido complex $(H_2O)_5Cr-CH_2C(O)NH_2^{2+}$, where the protonated carboxamide group has a $K_a = 0.071 \text{ M}$. It appears that these ligands may retain a high degree of anionic character.

For the sulfate dependent pathways, k_3 and k_4 , the latter is better defined for our experimental conditions. Although typically $k_3K_f[H^+] > k_4K_f$ for $[H^+] > 0.1 \text{ M}$, the sulfate dependent pathways are attenuated at the higher $[H^+]$, so that the k_1 pathway tends to dominate the k_3 pathway for these conditions. Scheme I presents the simplest possibility for these reactions, involving $(SO_4)(H_2O)_4Cr-R + H_2O$ for k_4 and $(SO_4)(H_2O)_4Cr-R + H_3O^+$ for k_3 . On this basis, one might expect some parallel between k_0 and k_4 and between k_1 and k_3 . Indeed, the ΔH^* for k_4K_f is in the same range as that for k_0 as expected if ΔH° for K_f is small. In our study¹⁴ in Chapter 5 on the effect of acetate, phosphate and methylphosphate anions on the heterolysis of these

compounds, the various kinetically equivalent alternatives for this reaction will be considered in detail. It is concluded that ions without ionizable hydrogens probably react by the nucleophilically attack on hydrogen atom of cis-water, while those with ionizable hydrogens may react by a bifunctional mode.

The situation with k_3 does not appear so simple. The values of ΔH^* for k_3K_f are generally much larger than ΔH_1^* and are more similar to ΔH_0^* . The values of k_3K_f are typically about 400 times larger than k_1 (see Table 2.4). This cannot be due to a large K_f because the kinetics establish that $K_f < 10$. The k_3K_f is larger because the higher ΔH^* is offset by a much more favorable ΔS^* . Earlier NMR studies¹³ indicate that protonation of a coordinated water in $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{X}$ complexes is not greatly different for $\text{X} = \text{N}_3^-$, CH_2CN^- or OH_2 . Therefore, pre-equilibrium formation of **I** should not be greatly favored by the presence of a coordinated sulfate ion, and this does not seem to be an explanation for the large k_3K_f values. It could be argued that the coordinated sulfate ion increases the negative charge on the $-\text{CH}_2$ group and promotes direct electrophilic attack of H_3O^+ on the $-\text{CH}_2$, so that the reaction is not proceeding through the intermediate analogous to **I**. Although direct electrophilic attack cannot be ruled out for the sulfate system, our previous study¹⁴ with phosphate species indicates that this is probably not the reaction pathway. It was found that species with ionizable protons are much better catalysts for heterolysis (e.g., $\text{HPO}_4^{2-} \gg (\text{CH}_3)\text{PO}_4^{2-}$). These observations suggest that species with ionizable protons, such as HSO_4^- in the present study, catalyse heterolysis by acting as bifunctional catalysts through an intermediate such as **III**. This gives eq 2.7 as a pathway that is kinetically equivalent to k_3 in Scheme I, but the sulfate ion dependent part of k_{obsd} (eq 2.4) must be modified by replacing $k_3K_fK_a$ by k_3' . With this change, the ΔH^* for k_3' is $\sim 6.5 \text{ kcal mol}^{-1}$ smaller than the values in Table 2.2 for k_3K_f and the ΔS^* is $\sim 26.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ more negative. Values of k_3' at 25°C are ~ 0.1 times those for k_3K_f in Table 2.4. It is possible to

compare the k_3' values of the benzyl complex with several oxyanions proposed¹⁴ to be reacting via **III**. The values of k_3' for HPO_4^{2-} , H_2PO_4^- , $(\text{CH}_3)\text{HPO}_4^-$ and HSO_4^- are 5.7×10^2 , 4.4×10^{-2} , 1×10^{-3} and $8.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, respectively. It appears that the



reactivity correlates predominantly with the basicity of the anion, which in turn implies that a critical part of the bifunctional catalysis lies in the ability of the anion to interact with the Cr(III) center. In **III**, this interaction is suggested to be via hydrogen bonding with the *cis*- H_2O ligand, although it could be a direct interaction with the metal center.

When we submitted this chapter for publication, a reviewer suggested that a *cis* coordinated sulfate could be the source of the catalysis, by analogy to *cis*-effects on ammonia loss from pentaamminechromium(III) complexes.¹⁵ The *cis*-complex could form by isomerization from the labile *trans* position, a process already studied by Sisley and Jordan^{7,8} for oxalate, phosphate and pyrophosphate reacting with $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{CN}^{2+}$. The previous work indicates that the *cis*-complex will coordinate another anion in the labile *trans* position so that the rate of Cr-C bond breaking would be second order in the anion. However no such term could be detected in our study¹⁴ of

the phosphate catalysed Cr–C bond breaking in benzyl complexes, nor in the current work with sulfate.

Experimental Section

Materials. The organic bromides were used as purchased (Aldrich). Stock solutions of NaClO_4 were analysed by passing an aliquot through a cation-exchange column in the H^+ form and titrating the liberated acid with standardized NaOH .

Solutions of the benzylpentaquachromium(III) complexes were prepared by mixing 40 mL of deoxygenated methanol containing 2 mmol of the appropriate benzyl bromide with 20 mL of aqueous 0.3 M chromium(II) perchlorate, prepared by amalgamated zinc reduction of aqueous chromium(III) perchlorate. After ~ 10 min at ambient temperature the solution had changed from pale blue to dark greenish yellow, and it was loaded onto a column (8×2 cm) of Dowex 50W-X2(200) ion exchange resin in either the H^+ or Na^+ form under an argon atmosphere at 0°C . Excess Cr(II) was eluted with 0.6 M NaClO_4 in 0.01 M HClO_4 , and the desired product was eluted with 1.0 M NaClO_4 in 0.01 M HClO_4 . The product was stored at -10 to -15°C .

Another way to prepare the complexes is the heterogeneous reaction by directly mixing aqueous chromium(II) perchlorate and the appropriate benzyl bromide under argon.⁴ Although the same product as in the above methanol-water medium was obtained, the reaction needs more than 4 h at room temperature with vigorous stirring, especially for solid cyanobenzyl bromides.

The chromium(II) used in the kinetic runs to suppress homolysis was commonly prepared from a stock solution of $\text{Cr}_2(\text{SO}_4)_3$ in perchloric acid by reduction with zinc amalgam. To test the sulfate effect, chromium(II) was prepared by reduction of aqueous $\text{Cr}(\text{ClO}_4)_3$.

Kinetic Measurements. The absorbance decrease was followed on a Hewlett Packard 8451 diode array spectrophotometer equipped with a thermostated cylindrical cell holder and standard water circulating temperature control system. A 50 mm path length cylindrical quartz cell with serum caps was used throughout. The data analysis typically involved 80 points over 5–6 half-lives, which were analysed by nonlinear least-squares to a first-order model. Solutions for kinetic runs were prepared by adding the required amounts of standardized sodium perchlorate and perchloric acid to the spectrophotometer cell. The cell was sealed with serum caps, placed in the thermostatted system, and deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) in varying amounts and the appropriate benzylchromium(III) complex at $\sim 1 \times 10^{-4}$ M. For the higher temperature runs (>65 °C), it was found advisable to avoid contact between the hot perchloric acid solution and stainless steel syringe needles. Teflon needles can be used to advantage under such conditions.

Reagent and Product Analysis. Chromium was determined spectrophotometrically as chromate, following oxidation with alkaline hydrogen peroxide.

The organic products were determined from reactant solutions containing 0.12 to 0.20 mmol ($(1.8\text{--}3.2) \times 10^{-3}$ M) of the appropriate benzylchromium(III) complex, 0.10 M HClO_4 and ~ 0.04 M Cr(II). The solutions were prepared at ambient temperature and sealed under argon in glass ampoules before bringing them to 65 °C in a water bath. Sealing is necessary to minimize evaporation and reaction with dioxygen. The solution changed from yellow to pale blue at completion, and was then exposed to air and extracted with 10 mL of chloroform. The organic extract was evaporated and then redissolved in CDCl_3 . The ^1H NMR spectrum was recorded on a

Bruker AM 300 system. The products were identified by comparison of their spectra to those of the commercially available substances.

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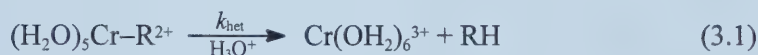
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Chapter 3. Kinetics of Homolysis of Substituted Benzyl Complexes of Pentaquachromium(III) and Product Variation with Substituent and Scavenger*

Introduction

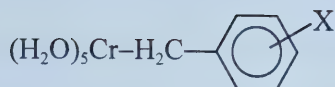
There is a wide range of η^1 organometallic derivatives of pentaquachromium(III)¹ with the general formula $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$. They decompose in aqueous acid by either heterolytic (eq 3.1) or homolytic (eq 3.2) cleavage of the chromium-carbon bond. The rates and relative importance of these processes vary



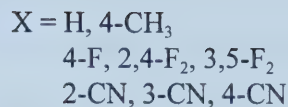
greatly with the nature of the R group. The homolysis process can be inhibited by the addition of aqueous chromium(II) which reacts rapidly with the $\text{R}\cdot$ radical to re-form the reactant. Then decomposition proceeds exclusively by the heterolytic pathway (k_{het}). On the other hand, scavengers can be added to irreversibly react with chromium(II) and/or $\text{R}\cdot$. Then decomposition proceeds by both heterolysis and homolysis, e.g. $k_{\text{obsd}} = k_{\text{homo}} + k_{\text{het}}$ and the homolytic reactivity can be determined if it is at least competitive with heterolysis.

The heterolysis of a series of substituted benzyl derivatives (**I**) of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ has been discussed in Chapter 2.² Homolysis of the H, 4- CH_3 , and 4-CN complexes

*A version of this chapter has been published. Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1994**, 33, 680–686.



(I)



was studied by Nohr and Espenson,³ but the kinetics were not corrected for heterolysis, and a peculiar acid dependence was suggested for the parent benzyl complex. Kita and Jordan⁴ studied the heterolysis and spontaneous decomposition kinetics of the benzyl complex.

In the present work, the homolysis of the above series of compounds is studied; the acid dependence and activation parameters have been determined, and organic product studies have been performed. The observation that the organic products depend on the nature of both the scavenger and the substituent on the benzyl ligand provides interesting information about the redox activity of these ligands. The interpretation of these results is aided greatly by recent electrochemical studies⁵ of substituted benzyl radicals. In two systems, two products are formed in competitive pathways in amounts which depend on the iron(III) scavenger concentration, and this allows us to calculate rate constants for reaction of the radicals with aqueous iron(III).

Results and Discussion

The observations from this study concern both the kinetics and the organic products of the homolysis reaction. The kinetic results are described first, because the organic products result from reactions subsequent to the rate-controlling Cr-C bond breaking in eq 3.2.

Kinetics. The decomposition of the various substituted benzyl derivatives of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ has been studied in the presence of several scavengers, namely dioxygen, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, aqueous iron(III), and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, with the latter two used mainly for the kinetic studies because of interferences arising from organic products with the other two. The temperature and acid dependence of the rate have been studied in the general range 20–35 °C and 0.01–0.9 M H^+ in 1.00 M $\text{NaClO}_4/\text{HClO}_4$, with the chromium(III) reactant at $(1-3) \times 10^{-5}$ M. The decomposition was monitored spectrophotometrically at an appropriate maximum for the reactant in the 300–362 nm region. The full kinetic results are given in Appendixes 3.1–3.15.

For all of the systems for which kinetic data are given, the decrease of absorbance with time in the presence of scavenger was first order and least-squares analysis gave the rate constant k_{obsd} . These values were corrected for heterolysis (k_{het}) to obtain the rate constant for homolysis (eq 3.3). The k_{het} values were calculated from the activation parameters previously determined² (see Chapter 2). This correction is

$$k_{\text{homo}} = k_{\text{obsd}} - k_{\text{het}} \quad (3.3)$$

small (2%) for all systems except the more heterolytically reactive 2-cyano complex where it is <6%, and the 4-cyano complex where it is 30 to 50%, depending on the acidity. The kinetics of the latter system are discussed separately below. For all the systems, k_{homo} is essentially independent of the nature of the scavenger and independent of the concentration of H^+ except for the 4-cyano complex.

The 4-cyano complex is somewhat different because the rate law for heterolysis shows a saturation effect with $[\text{H}^+]$ described by eq 3.4. This rate law is consistent with pre-equilibrium protonation of the complex with an acid dissociation

$$k_{\text{het}} = \frac{K_{\text{aCN}}k_0 + k_1[\text{H}^+]}{K_{\text{aCN}} + [\text{H}^+]} \quad (3.4)$$

constant (K_{aCN}) and specific rate constants k_0 and k_1 for heterolysis of the unprotonated and protonated forms, respectively. The temperature dependence of these values was determined² between 25 and 43 °C, and $K_{\text{aCN}} = 3.15 \times 10^{-2}$ M at 25 °C. One would expect the homolysis to show a similar saturation effect with $[\text{H}^+]$, but k_{homo} appears to be almost independent of $[\text{H}^+]$ as can be seen from representative results at 25 °C in Table 3.1. The kinetic observations for the heterolysis and homolysis seem to be internally consistent only if the rate constants for homolysis of the unprotonated (k_0°) and protonated (k_1°) forms are almost identical. Inspection of all of the data reveals that there is a small trend to higher values of k_{homo} at lower acidity. The temperature and $[\text{H}^+]$ dependencies of k_{homo} have been fitted to the form of eq 3.4 with k_0° and k_1° replacing k_0 and k_1 , respectively, and K_{aCN} fixed at values determined from the heterolysis study. It has been possible to extract values of k_0° and k_1° and their temperature dependence as given in Table 3.2.

The rate constants and activation parameters for all the systems are summarized in Table 3.2. The values are given independently for the two scavengers, Fe(III) and $(\text{NH}_3)_5\text{CoBr}^{2+}$, to show that there are no substantial or persistent differences. The rate constants at 25 °C change by about a factor of 20 from the most reactive 4-methyl to the least reactive 3-cyano system, and this is due largely to a small increase in $\Delta H^\ddagger$ from about 26 to 30 kcal mol⁻¹ with $\Delta S^\ddagger$ values of ~ 22 cal mol⁻¹ K⁻¹. Large positive $\Delta S^\ddagger$ values are typical of homolysis reactions¹ of $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ complexes. The rate constants for the 4-methyl and benzyl complexes are in reasonable agreement with the values of 3.7×10^{-3} and 2.6×10^{-3} s⁻¹ determined by Nohr and Espenson.³ Their value of 5.56×10^{-4} s⁻¹ for the 4-cyano complex is

Table 3.1. Kinetic Results for the Homolysis of 4-Cyanobenzylpenta-aquachromium(III) at 25 °C in 1.00 M HClO₄/NaClO₄.

Scavenger	[H ⁺] M	10 ⁴ × <i>k</i> _{obsd} s ⁻¹	10 ⁴ × <i>k</i> _{homo} , s ⁻¹	
			Obsd ^a	Calcd ^b
O ₂ (air)	0.010	5.170	4.17	4.08
	0.020	5.260	4.03	3.96
	0.0298	5.260	3.85	3.88
	0.0398	5.330	3.85	3.82
	0.0596	5.345	3.72	3.75
	0.0990	5.300	3.51	3.66
	0.248	5.660	3.68	3.55
	0.346	5.450	3.43	3.53
	0.595	5.690	3.62	3.60
	0.573	5.730	3.63	3.49
Fe(III)	0.0230	5.349	4.07	3.94
	0.0420	5.368	3.86	3.81
	0.0610	5.517	3.88	3.74
	0.100	5.571	3.78	3.66
	0.241	5.742	3.77	3.56
	0.336	5.731	3.71	3.53
	0.573	5.734	3.66	3.50
	0.857	5.765	3.67	3.49
Co(NH ₃) ₅ Br ²⁺	0.0230	4.758	3.48	3.94
	0.0424	5.053	3.55	3.81
	0.0610	4.952	3.32	3.74

Table 3.1. continued

Scavenger	[H ⁺]	$10^4 \times k_{\text{obsd}}$ s ⁻¹	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
	M		Obsd ^a	Calcd ^b
Co(NH ₃) ₅ Br ²⁺	0.100	5.045	3.26	3.66
	0.336	5.117	3.10	3.53
	0.573	5.327	3.26	3.50
	0.857	5.475	3.38	3.49

^a Calculated by subtraction of the heterolysis rate constant from k_{obsd} . ^b Calculated from the rate law described in the text, and the ΔH^* and ΔS^* values given in Table 3.2.

Table 3.2. Summary of the Rate Constants and Activation Parameters for the Homolysis of Substituted Benzyl Complexes of Pentaquachromium(III)

Substituent	Scavenger	Hammett σ	$10^3 \times k_{\text{homo}}$ $\text{s}^{-1}(25^\circ\text{C})^a$	ΔH^{*b} kcal mol^{-1}	ΔS^{*b} $\text{cal mol}^{-1} \text{K}^{-1}$
4-CH ₃	Co(NH ₃) ₅ Br ²⁺	-0.14	4.05	27.1 ± 1.0	21.5 ± 3.3
	Fe(III)		4.15	25.9 ± 0.6	17.3 ± 2.0
H	Co(NH ₃) ₅ Br ²⁺	0	2.07	27.3 ± 1.2	20.6 ± 4.0
	Fe(III)		2.03	26.9 ± 0.5	19.3 ± 1.6
4-F	Co(NH ₃) ₅ Br ²⁺	0.06	1.87	27.6 ± 1.1	21.6 ± 3.7
	Fe(III)		1.78	27.3 ± 0.9	20.4 ± 3.1
2,4-F ₂	Co(NH ₃) ₅ Br ²⁺	0.60	0.516	28.3 ± 0.5	21.2 ± 1.7
	Fe(III)		0.498	28.9 ± 1.4	23.4 ± 4.5
3,5-F ₂	Co(NH ₃) ₅ Br ²⁺	0.68	0.278	28.7 ± 1.0	21.6 ± 3.2
3-CN	Co(NH ₃) ₅ Br ²⁺	0.62	0.223	30.0 ± 1.2	25.5 ± 4.0
	Fe(III)		0.249	29.3 ± 1.4	23.1 ± 4.6
2-CN	Co(NH ₃) ₅ Br ²⁺	1.06	0.346	29.1 ± 0.7	23.2 ± 2.4
	Fe(III)		0.377	29.3 ± 1.3	23.9 ± 4.3
	Co(NH ₃) ₅ Cl ²⁺		0.369	29.0 ± 0.6	23.1 ± 2.0
4-CN ^c	Fe(III), Co(NH ₃) ₅ Br ²⁺	0.70	0.428(k_0°)	30.6 ± 0.4	28.6 ± 3.2
	Fe(III), Co(NH ₃) ₅ Br ²⁺		0.346(k_1°)	30.1 ± 0.3	26.6 ± 2.0

^a Calculated from ΔH^* and ΔS^* for each scavenger. ^b Calculated for each scavenger; errors are 95 % confidence limits. ^c The data for the two scavengers were analysed together to determine k_0° and k_1° .

consistent with our k_{obsd} values (Table 3.1), but they were unaware of the substantial heterolysis correction so that the true homolysis rate constants are smaller.

Nohr and Espenson noted a correlation of k_{homo} and the Hammett substituent constant σ . The latter are also given in Table 3.2, and the correlation now is not as good with the expanded and corrected data base and the inclusion of *ortho*- and *meta*-substituted systems. If the results of Nohr and Espenson for the 4-bromo and 4-(trifluoromethyl) complexes are included, it appears that the 3-cyano and 3,5-difluoro complexes are reacting too slowly and the 2-cyano complex reacts too fast. If the latter three system are excluded, one finds $\log(k_{\text{homo}}) = -2.62 - 1.06\sigma$ ($r = 0.985$) as shown in Figure 3.1. For the three deviant systems, the predicted and observed rate constants differ by about a factor of 2.

It is interesting to note that the stability of the benzyl radical does not seem to be a determining factor in the homolysis rate. Various measures of substituted benzyl radical stability^{6,7} (σ^* values)⁸ indicate that, relative to the benzyl radical, the 3-cyano should be less stable and the 4-cyano more stable. If the stability of the radical were contributing significantly to the stability of the transition state, one would expect the 4-cyano complex to homolyze more rapidly and the 3-cyano complex less rapidly than the benzyl. This is certainly not true.

There is a reasonable correlation of the rate constants for heterolysis and homolysis of these benzyl systems. For six of the eight systems in Table 3.2, $\log(k_{\text{homo}}) = 5.46 + 1.51 \log(k_{\text{het}})$ ($r = 0.985$; k_{het} is the H^+ independent value; rate constants at 25 °C) as shown in Figure 3.2. This implies that the strength of the Cr–C bond is important for both processes. The two exceptions to this correlation are the 2-cyano and 4-cyano complexes which undergo heterolysis faster than predicted by 10 and 50 times, respectively. The larger heterolysis rates were attributed² to delocalization of negative charge from CH_2 onto the CN substituent thereby weakening the Cr–C bond.

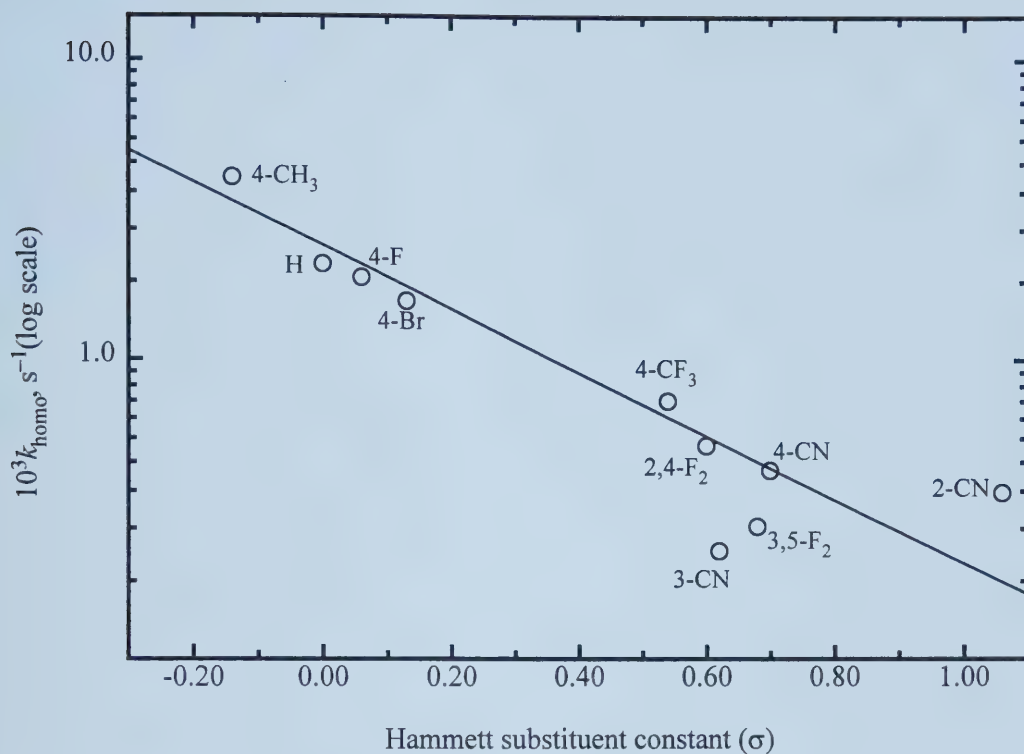


Figure 3.1. A plot illustrating the LFER correlation of k_{homo} with the Hammett σ substituent constant; $\log(k_{\text{homo}}) = -2.62 - 1.06\sigma$ ($r = 0.985$) (3-CN, 2-CN and 3,5-F₂ are excluded from the correlation).

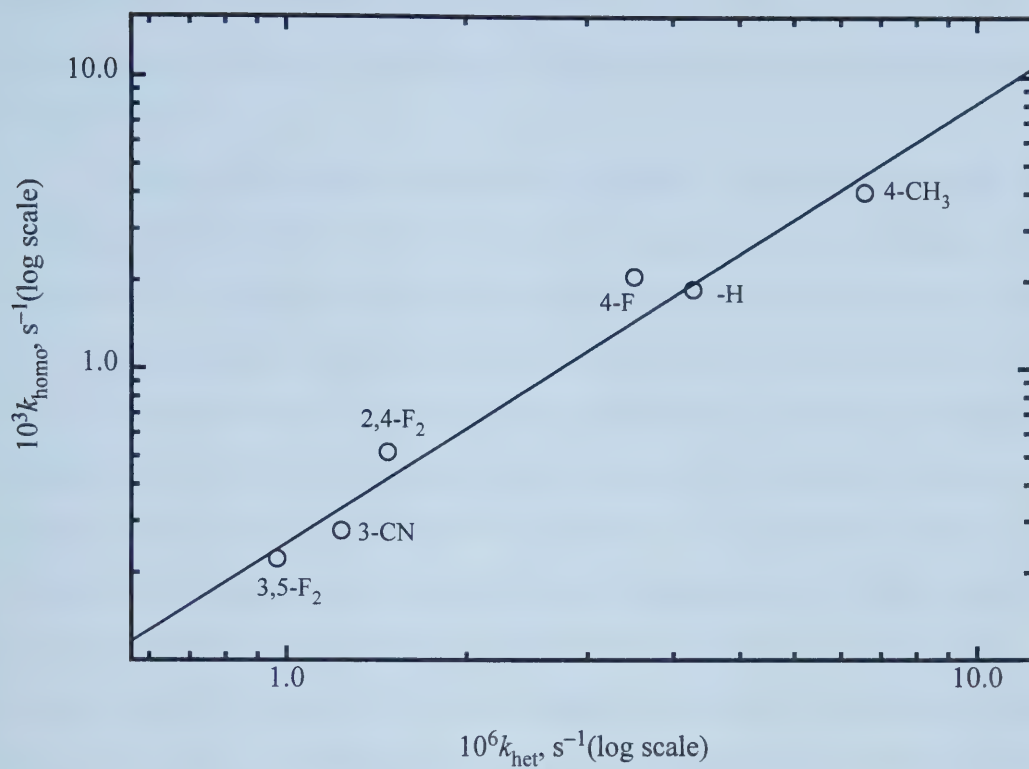


Figure 3.2. A correlation of the rate constants for heterolysis (k_{het}) and homolysis (k_{homo}); $\log(k_{\text{homo}}) = 5.46 + 1.51 \log(k_{\text{het}})$ ($r = 0.985$)

For homolysis, this effect may be attenuated if homolysis is viewed as also involving electron transfer from the R^- ligand to Cr^{III} . The electron transfer would be disfavoured by delocalization.

It was noted above that dioxygen and $(NH_3)_5CoCl^{2+}$ were not used regularly as scavengers for the kinetic studies because of organic product interference. For $(NH_3)_5CoCl^{2+}$, the bibenzyl product tends to precipitate during the kinetic runs, and this scavenger could only be used with the cyano derivatives. With dioxygen, we often observed that the first-order rate constant appeared to be somewhat wavelength dependent in the 280–320 nm region. This was especially a problem for the cyano systems whose absorbance maxima² are below 320 nm. The problem is due to a second process which is clearly manifested by observations in the 240–260 nm region, where an initial increase in absorbance is followed by a decrease, as shown for the 2-cyano complex in Figure 3.3. We have made some attempt to deconvolute these processes by fitting absorbance-time data at four wavelengths (typically 244, 256, 284, and 316 nm) to a biphasic model. The general conclusion is that the faster process is homolysis as judged from the correspondence of the rate constant to that with other scavengers (see Table 3.1) and from observations at wavelengths in the 350–360 nm range. The second process has $k = 2 \times 10^{-4} \text{ s}^{-1}$ at 25 °C for both the 2- and 4-cyano complexes and we suspect that this process involves decomposition of CrO_2^{2+} (formed from $Cr^{2+} + O_2$; see below), because the rates we observe are quite similar to those indicated by the absorbance-time curves reported by Brynildson, Bakac, and Espenson⁹ for the decomposition of CrO_2^{2+} in the presence of dioxygen. In addition, CrO_2^{2+} has significant absorbance at the $2 \times 10^{-5} \text{ M}$ concentrations of this study and in the 240–300 nm range where we observe these complications. These are not ideal systems for studying CrO_2^{2+} because of the absorbance of the aromatic products, but

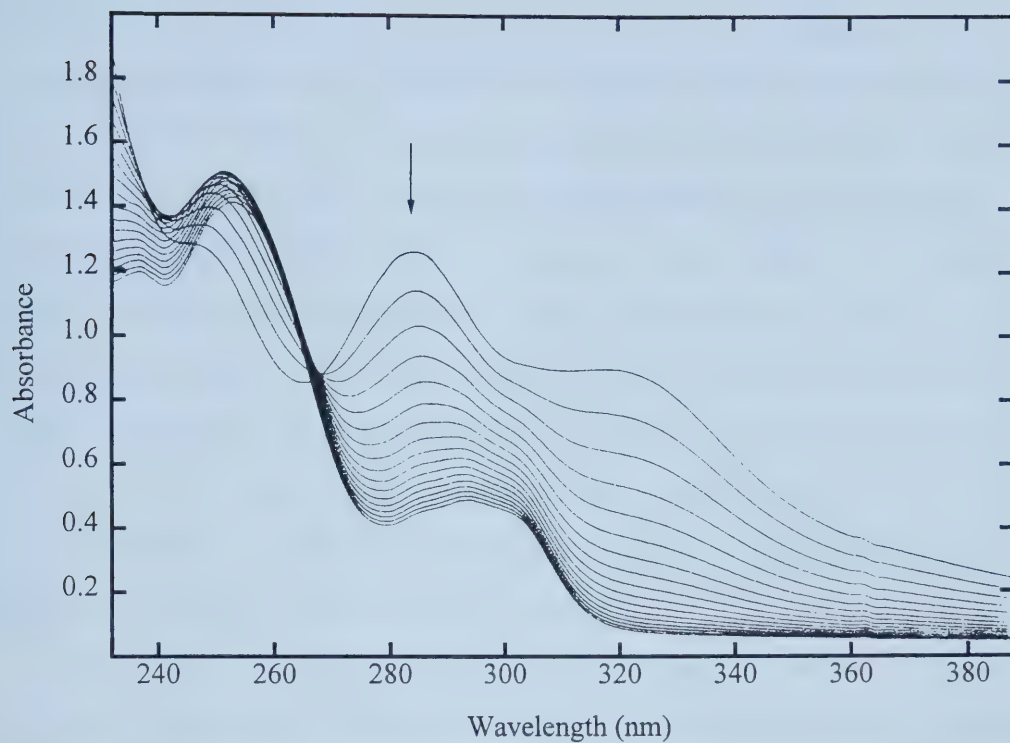


Figure 3.3. Variation of absorbance with time and wavelength for the 2-cyanobenzyl-pentaaquachromium(III) complex with air (25 °C, 0.10 M H⁺).

homolysis of other Cr–R complexes could be adapted to the preparation of CrO_2^{2+} because it avoids the presence of excess Cr(II) which leads to decomposition of CrO_2^{2+} .

Organic Products. The organic products have been identified by ^1H NMR after extraction into chloroform, as described in the experimental section, and relative amounts have been determined from the integrated NMR intensities. The chemical shifts of the most diagnostic protons for each product are given in Table 3.3. The reactions were done in 0.10 M HClO_4 with $(1.8\text{--}3.2) \times 10^{-3}$ M chromium and the oxidant concentration varied typically in the range of 3–15 times the chromium, except for the air saturated solutions which had an O_2 concentration of $\sim 3 \times 10^{-4}$ M. The stoichiometry with respect to the oxidant scavenger has been determined for $(\text{NH}_3)_5\text{CoCl}^{2+}$, aqueous iron(III), and $(\text{NH}_3)_5\text{CoBr}^{2+}$.

The product results are summarized in Table 3.4, and the stoichiometry results are given in Appendix 3.16. The stoichiometries are consistent with the product results and are close to 2 moles of scavenger per mole of chromium, unless bibenzyl is formed when the ratio reduces to 1:1 in the limit of 100 % bibenzyl formation. The results are ordered in Table 3.4 in such a way as to show trends in the type and percentage of products.

Scavenging with dioxygen is the simplest experiment to carry out, but there are problems because of the limited solubility of O_2 in water¹⁰ ($\sim 1.6 \times 10^{-3}$ M at 1 atm O_2). This may make dissolved dioxygen in deficiency at chromium concentrations and solution volumes compatible with product recovery. Bubbling O_2 or air through the solution risks removal of volatile products such as benzaldehyde.

Dioxygen gives the aldehyde as the major product in all cases, but there is a substantial amount of alcohol with the 4-methyl complex, equal amounts (9 %) of bibenzyl and alcohol from the benzyl complex, and small amounts (5–10 %) of alcohol in three other systems. The potential diversity of reactions makes an

Table 3.3. Chemical Shifts of Diagnostic Proton Resonances in the Organic Reaction Products

Reactant	Product Functional Group ^a				
Substituent	CH ₃	(C ₂ H ₄)	HCO	CH ₂ (OH) ^d	CH ₂ Br
4-CH ₃	2.31 ^b	2.87	9.96 ^b	4.60(2.16)	4.52 ^c
H	2.35 ^c	2.95 ^c	10.03 ^c	4.70(1.77) ^c	4.51 ^c
4-F	2.35	2.87	9.96	4.65(1.93)	4.48 ^c
2,4-F ₂	2.24	2.88	10.28 ^c	4.72(1.70)	4.49 ^c
3,5-F ₂	2.35	2.89	9.95 ^c	4.67(2.07) ^c	4.40 ^c
2-CN	2.58 ^b	3.17	10.34 ^b		4.64 ^c
3-CN	2.39 ^b	2.97	10.05 ^b		4.47 ^c
4-CN	2.41 ^b	3.00	10.11 ^b		4.48 ^c

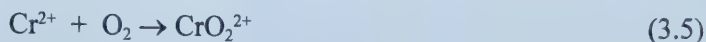
^a Chemical shifts in ppm relative to internal TMS in CDCl₃. ^b Identified by comparison to data for the compound in the Aldrich compilation. ^c Identified by comparison to spectra of commercial samples. ^d OH values in parentheses.

Table 3.4. Summary of Products with Various Scavengers for Analysis of Substituted Benzopermanganate(III) Complexes in 1:10 to 5:100, at Ambient Temperature. Products Are the Corresponding Benzoyl (PhCH_2), Alkyl (PhCH_2OH), Aldehyde (PhCHO), Bromide (PhCH_2Br), and Methyl (PhCH_3) Derivatives, with Percentages Given in Parentheses

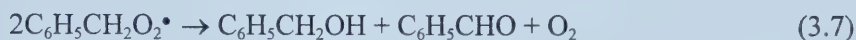
Reagent	Scavenger			
	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}^a$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}^a$	PhCH_3	$\text{C}_6\text{H}_5\text{CHO}$ mmHg
4-Cl $^-$	PhCH_2OH 100	PhCH_2OH 100	PhCH_2OH 100	PhCHO (70) PhCH_2OH (30)
4-F $^-$	PhCH_2OH 100	PhCH_2OH 100	PhCH_2OH 100	PhCHO (95) PhCH_2OH (5)
H	PhCH_2OH 100	PhCH_2OH >99 b PhCH_2Br <1	PhCH_2OH 71-98 b PhCH_2Br (31-2)	PhCH_2OH (9) PhCHO (40) PhCH_2Br (9)
1,4-F $^-$	PhCH_2OH 100	PhCH_2OH 100	PhCH_2OH 51-45 b PhCH_2Br (44-5)	PhCHO (32) PhCH_2OH (1)
1,5-F $^-$	PhCH_2OH 100	PhCH_2OH (51-45) b PhCH_2Br (45-55) PhCH_2Br (5-0)	PhCH_2OH 100	PhCHO (50) PhCH_2OH (9)
1-Cl $^-$	PhCH_2OH 100	PhCH_2Br (4-5) b PhCH_2Br (>0)	PhCH_2OH 100	PhCHO (9-8) b PhCH_2Br (>0)
1-Cl $^-$	PhCH_2OH 100	PhCH_2Br (96)	PhCH_2OH 100	PhCHO (>98) b PhCH_2Br (<1)
4-Cl $^-$	PhCH_2OH (50) PhCH_2Br (6)	PhCH_2Br (50) PhCH_2Br (6)	PhCH_2OH (74-6) PhCH_2Br (24-20)	PhCHO (85) PhCH_2Br (5)

a Total amount of the minor product could not be quantified. b The product distribution varied with increasing reagent concentration in the direction given.

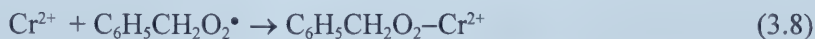
explanation of the products problematic. The primary homolysis products are expected to react with O_2 via reactions 3.5 and 3.6, with $k > 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.^{8,11,12} The CrO_2^{2+}



species is relatively stable⁹ at modest concentrations, and the benzyl peroxy radical is much more reactive. The standard chemistry of the peroxy radical^{12,13} suggests that it would undergo the equivalent of disproportionation (eq 3.7). The formation of small amounts of alcohol relative to aldehyde, rather than equal amounts, implies that disproportionation is generally a minor pathway.

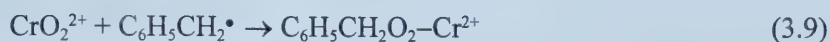


Direct reaction of Cr^{2+} and the peroxy radical (eq 3.8) appears unlikely because it involves a bimolecular reaction between transient intermediates. However, at the

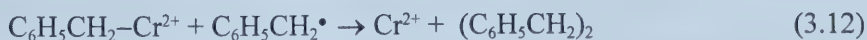


rather low O_2 concentrations, this reaction could be competitive with eq 3.5, since the peroxy radical might recombine with its parent Cr^{2+} before the latter reacts with a second O_2 . The chromium(III) organoperoxy complex product of eq 3.8 could form in other ways, such as eq 3.9, but this does not seem to be highly important because our observations indicate that CrO_2^{2+} is decomposing at its normal spontaneous rate as a product of the homolysis. Another pathway for producing this complex is given by eq

3.10, which is analogous to that proposed by Ryan and Espenson¹⁴ for the Cr-(isopropyl)²⁺ + O₂ system. This pathway is a chain reaction with C₆H₅CH₂• as a chain carrier and the decomposition rate of C₆H₅CH₂-Cr²⁺ with O₂ should be faster than with other scavengers. Therefore, this pathway is insignificant because our experimental results show that the decomposition rate of C₆H₅CH₂-Cr²⁺ is the same for all of scavengers. In any event, the peroxy complex could decompose to aldehyde via eq 3.11. These reactions can account for the aldehyde and alcohol products.



The formation of 9 % bibenzyl by the parent benzyl complex, and the traces of analogous products with the 2- and 3-cyano complexes requires further explanation. This would normally be explained by dimerization of two benzyl radicals, but the low concentrations and short lifetimes of these radicals in the presence of dioxygen makes dimerization unlikely. Although Nohr and Espenson³ reported no bibenzyl from this reaction, Kita and Jordan⁴ found 10%, in agreement with the 9% found in this study. Kita and Jordan suggested that the bibenzyl might form by eq 3.12 in competition with scavenging by O₂. However, this possibility must be withdrawn because it has



untenable implications for other scavengers. For example, $(\text{NH}_3)_5\text{CoCl}^{2+}$ gives exclusively bibenzyl, but if this were formed only by reaction 3.12, then the homolysis rate constant should be twice that with other oxidants which do not yield bibenzyl because eq 3.12 results in the loss of two moles of reactant per homolysis event. Nohr and Espenson found the same rate constant for the benzyl complex with $(\text{NH}_3)_5\text{CoCl}^{2+}$ and iron(III), and we observe the same result with several substituted benzyl complexes. We now suspect that the bibenzyl may form at very low O_2 concentrations, such as towards the end of the reaction, or trace amounts may be introduced during handling of the stock reactant solutions.

It should be noted that we also observed small (<5%) and variable amounts of a product with an ^1H resonance near 4.9 ppm. This is tentatively assigned to the dibenzyl peroxide derivative, for which the parent benzyl compound has the CH_2 resonance at 4.83 ppm in CCl_4 .¹⁵ This could form by reaction 3.13. More of this



product, relative to bibenzyl, is formed with air compared to pure O_2 as the scavenger source. This indicates that dimerization in reaction 3.13 is competitive with reaction 3.6 at typical O_2 concentrations.

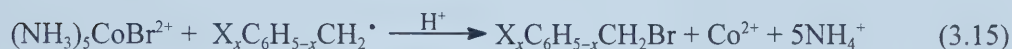
Homolysis in the presence of $(\text{NH}_3)_5\text{CoCl}^{2+}$ always proceeds with production of one cobalt(II) per chromium and produces only the bibenzyl derivative. The latter must form by dimerization of two $\text{X}_x\text{C}_6\text{H}_{5-x}\text{CH}_2^\bullet$ radicals and this process must be more efficient than oxidation of the radical by $(\text{NH}_3)_5\text{CoCl}^{2+}$. Nohr and Espenson also found only bibenzyl from the reaction of $(\text{NH}_3)_5\text{CoCl}^{2+}$ and $\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$.

Rather surprisingly, just changing the oxidant to $(\text{NH}_3)_5\text{CoBr}^{2+}$ gives entirely different products, and the stoichiometry is always two cobalt(II) produced per

chromium. The first four complexes in Table 3.4 give >98 % alcohol, indicating that $(\text{NH}_3)_5\text{CoBr}^{2+}$ oxidizes these radicals effectively in competition with dimerization. The oxidized radical, $\text{X}_x\text{C}_6\text{H}_{5-x}\text{CH}_2^+$ will react with water to give the alcohol, with the overall reaction of eq 3.14.



With the 3,5-difluoro complex, the situation becomes more complex and the products are on average 50 % alcohol and 50 % organic bromide. This implies that outer-sphere (eq 3.14) and inner-sphere (eq 3.15) oxidation are competitive processes



for the 3,5-difluorobenzyl radical. The cyano substituted benzyis all give the bromide as the dominant product. Espenson and co-workers have reported that the cyclopentyl¹⁶ and isopropyl¹⁴ radicals also react with $(\text{NH}_3)_5\text{CoBr}^{2+}$ by an inner-sphere mechanism, and the ethyl radical¹⁷ reacts with both $(\text{NH}_3)_5\text{CoBr}^{2+}$ and $(\text{NH}_3)_5\text{CoCl}^{2+}$ by this mechanism. The ethyl radical reacts 6.4×10^{-3} more slowly with $(\text{NH}_3)_5\text{CoCl}^{2+}$ than with $(\text{NH}_3)_5\text{CoBr}^{2+}$, and this reactivity difference might explain the lack of an inner-sphere product with $(\text{NH}_3)_5\text{CoCl}^{2+}$.

The lack of outer-sphere reactivity of $(\text{NH}_3)_5\text{CoCl}^{2+}$ is more difficult to rationalize. With typical outer-sphere reductants such as $\text{Cr}(\text{bipy})_3^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$, $(\text{NH}_3)_5\text{CoCl}^{2+}$ has about a 7 times smaller rate constant than $(\text{NH}_3)_5\text{CoBr}^{2+}$. Simple Marcus theory¹⁸ implies that a similar reactivity difference would be expected for reducing agents such as the benzyl radicals. However, the more detailed analysis

described below indicates that $(\text{NH}_3)_5\text{CoCl}^{2+}$ is at least 10^3 times less reactive than $(\text{NH}_3)_5\text{CoBr}^{2+}$ with the benzyl radicals.

With aqueous iron(III) as the oxidant, the products indicate that the first two radicals in Table 3.4 undergo outer-sphere oxidation. For the benzyl and 2,4-difluorobenzyl radicals, oxidation and dimerization are competitive processes and product distribution varies with the oxidant concentration. These results are analysed further below. The last 4 species in Table 3.4 give only dimerization. This pattern seems consistent with the thermodynamic oxidizability trends of the radicals, based on the polarographic data in acetonitrile.⁵ However, these data give the reduction potential for $\text{C}_6\text{H}_5\text{CH}_2^+$ as 0.73 V (in acetonitrile vs. SCE) which can be converted¹⁹ to ~ 0.98 V vs. the NHE. On this basis, $\text{Fe}(\text{OH}_2)_6^{3+}$, with an $E^\circ \approx 0.75$ V, should not be able to oxidize $\text{C}_6\text{H}_5\text{CH}_2^\bullet$. The same argument applies to the 4-fluoro system for which $E^\circ = 0.73$ V (in acetonitrile vs. SCE). The E° for the 3- and 4-cyano systems⁵ are > 1 V, and these radicals should not be oxidized by $\text{Fe}(\text{OH}_2)_6^{3+}$, consistent with the products. A more realistic analysis should take into account that solvation will make the carbocations less reducible in water than in acetonitrile, so that the E° values in acetonitrile, corrected to the NHE scale, are all too positive. In fact, it appears that this correction (~ 0.25 V) is about the magnitude which the solvation contribution makes, so that the E° vs. SCE in acetonitrile may be about the correct value in water vs. NHE.

For the reaction of iron(III) with the benzyl and 2,4-difluorobenzyl complexes, the product distribution depends on the iron(III) concentration and further details are given in Table 3.5. It should be noted that the isolated product ratio agrees with that predicted from the stoichiometry also given in Table 3.5. These observations can be understood from Scheme I as due to competition between dimerization (k_2) and oxidation (k_3) since higher iron(III) concentrations give more of the alcohol oxidation product. To quantitatively analyse the system, we have used numerical integration

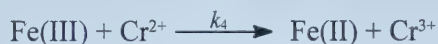
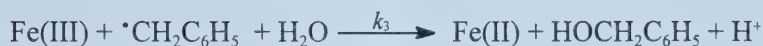
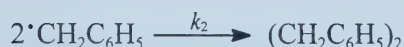
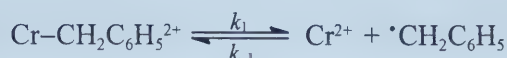
Table 3.5. Summary of Products and Stoichiometry for Systems Where Product Distribution Depends on the Iron(III) Oxidant Concentration in 0.10 M HClO₄ at Ambient Temperature.

Substituent	10 ³ [Cr-R ²⁺]	10 ³ [Fe(III)]	[Fe(II)]/[Cr] ^a	% ROH ^b	
	M	M		Obsd ^c	Calcd ^d
H	3.10	9.30	1.72 ^e	70(72)	73.3
	3.10	18.6	1.90	88(90)	88.8
	3.10	27.9	2.02	>98(100)	94.1
2,4-F ₂	3.20	9.60	1.50	51(50)	50.7
	3.20	19.2	1.68	(68) ^f	71.4
	3.20	28.8	1.80	85(80)	81.9

^a Stoichiometry ratio of Fe(II) produced to initial Cr-R. ^b The other product is the bibenzyl derivative as given in Table 3.4. ^c Value from NMR integration of CHCl₃ extracts and values predicted from the stoichiometry ratio in parentheses. ^d Calculated from Scheme I with rate constants given in the text. ^e Experiments in 0.44 and 0.94 M HClO₄ gave only slightly different ratios of 1.71 and 1.68, respectively. ^f Products were not determined by NMR.

based on the reactions in Scheme I. The known rate constants are $k_1 = k_{\text{hom}}$, determined in this work, and k_4 determined by Dulz and Sutin.²⁰ The colligation rate constant k_{-1} is $8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.²¹ The rate constant k_2 for the benzyl radical ($-\text{d}[\text{R}\cdot]/\text{dt} = 2k_2[\text{R}\cdot]^2$) has been determined as 1.55×10^9 (aqueous 0.1 M *tert*-butyl alcohol),²² 2.5×10^9 (aqueous *tert*-butyl alcohol, pH 7.5)²³ and $1.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (aqueous 0.2 M *tert*-butyl alcohol, pH 7.0).²⁴ We have used $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as a reasonable estimate for k_2 .

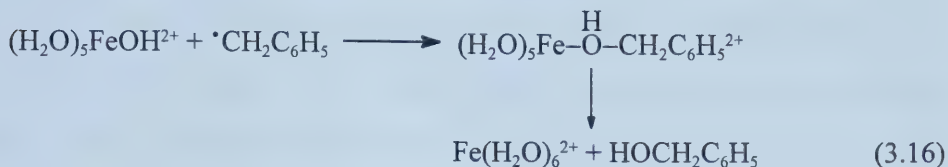
Scheme I



The product distributions have been calculated for the various concentration conditions with the assumption that k_2 and k_{-1} are the same for the benzyl and 2,4-difluorobenzyl radicals and that only k_3 is different. Reasonable agreement of calculated and experimental values can be obtained, as shown by the results in Table 3.5, with k_3 values of 1.8×10^4 and $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for the benzyl and 2,4-difluorobenzyl radicals, respectively.

It seems likely that oxidation of a radical by aqueous iron(III) to give an alcohol is an outer-sphere reaction. However, there is a potential inner-sphere pathway involving hydrolysed iron(III) with OH^- acting as the bridging ligand, as shown in eq

3.16. If alcohol is the only product, it is difficult to test this possibility because one needs to measure directly the rate of reaction 3.16 as a function of $[H^+]$. However, with



oxidation and dimerization in competition, as for the benzyl radical, the fraction of alcohol product should decrease with increasing acidity if the inner-sphere pathway (eq 3.16) is operative. We find that the products, as judged from the stoichiometry, do not vary when the $[H^+]$ is changed from 0.10 to 0.94 M (see footnote to Table 3.5). Therefore, eq 3.16 is not operative for these systems.

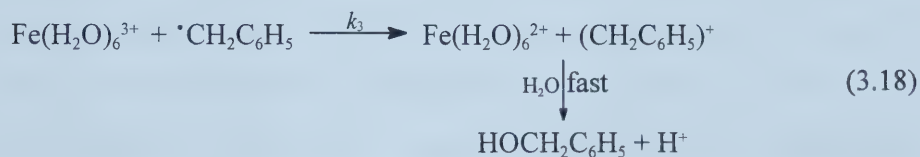
Another possible inner-sphere mechanism is shown by eq 3.17. This is an example of what Espenson²⁵ has called a colligation reaction, although it has aspects of



an oxidative addition and formally gives an Fe(IV) complex of the benzyl anion. Such reactions are observed for M(II) ions (Cr(II),¹ V(II),²⁶ Co(II) complexes,^{27,28} Fe(II)-NTA complexes,²⁸ Ni(II) complexes²⁵) which have a normally accessible M(III) oxidation state. They also have been observed for aqueous Cu(II)^{29,30} and some of its complexes.³¹ The reaction of aqueous Cu(II) with the benzyl radical³⁰ has $k = 2.1 \times 10^7$ M⁻¹ s⁻¹ and the $(Cu^{III}-CH_2C_6H_5)^{2+}$ product decomposes to benzyl alcohol and Cu(I), rather than Cu(III) and toluene. Cohen and Meyerstein²⁸ have suggested that the NTA ligand is necessary in the Fe(II) system, for example, because it labilizes the coordinated water for substitution. The modest water exchange rate of $Fe(OH_2)_6^{3+}$ ($k_{ex} =$

$1.6 \times 10^2 \text{ s}^{-1}$, 25°C),³² and the fact that $\text{Fe}(\text{OH}_2)_6^{4+}$ is unknown make eq 3.17 an unattractive alternative. One would have expected this pathway to show an $[\text{H}^+]^{-1}$ dependence because of the greater lability of $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ ($k_{\text{ex}} = 1.2 \times 10^5 \text{ s}^{-1}$, 25°C),³² but the amount of alcohol formed from the decomposition of the product of eq 3.17 shows no $[\text{H}^+]$ dependence, as already noted. Furthermore, the more oxidizing radicals, such as 4-cyanobenzyl compared to 4-fluorobenzyl¹⁵, should favor eq 3.17 and produce more alcohol, but the opposite is actually observed.

One is left with the outer-sphere oxidation mechanism of eq 3.18 as the most probable source of the alcohol product. This can be tested by using Marcus theory¹⁸ to estimate the rate constant k_3 , which will be the rate controlling process in eq 3.18. If



one assumes that k_{22} , the electron exchange rate constant for $\text{PhCH}_2\cdot + \text{PhCH}_2^+$, is $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and that the E° values in acetonitrile (vs SCE) are equal to the values in water (vs. NHE), then k_3 ($= k_{12}$)¹⁸ is calculated to be $0.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, in reasonable agreement with 1.8×10^4 calculated from the product distribution. Similar calculations for the 4-methyl and 3-CN radicals give k_3 values of 2.6×10^5 and $2.7 \text{ M}^{-1} \text{ s}^{-1}$, respectively. These are consistent with >99 % oxidation of the former and >99 % bibenzyl formation in the latter.

If the outer-sphere mechanism is also operative for $(\text{NH}_3)_5\text{CoBr}^{2+}$, then the dominant or substantial formation of alcohol compared to bibenzyl for the first four substituents in Table 3.4 implies that it oxidizes these radicals with $k_3 > 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, assuming that the rate constant for bibenzyl formation is essentially independent of

the substituent. The situation changes at the 3,5-difluoro complex which yields similar amounts of alcohol and bromide and small to negligible amounts of bibenzyl derivative. This requires that the rate constants for the outer-sphere and inner-sphere reactions are $\sim 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Then for the more difficult to oxidize cyano systems, only the inner-sphere product is observed.

The same analysis applied to the results with $(\text{NH}_3)_5\text{CoCl}^{2+}$ indicates that $k_3 \leq 10^2 \text{ M}^{-1} \text{ s}^{-1}$ in order to explain the absence of oxidation product, and the inner-sphere rate constant must be of the same or smaller magnitude to explain the absence of inner-sphere product. Therefore, for the most easily oxidized 4-methylbenzyl radical, $(\text{NH}_3)_5\text{CoCl}^{2+}$ is at least 10^3 times less reactive than $(\text{NH}_3)_5\text{CoBr}^{2+}$. This may be contrasted with the normal outer-sphere reactivity difference of ~ 7 for these complexes with $\text{Cr}(\text{bipy})_3^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ and with the strongly reducing radical $\bullet\text{C}(\text{CH}_3)_2\text{OH}$.³³ On the basis of the reasonable success of the simple Marcus equation in predicting the radical reactivity with $\text{Fe}(\text{OH}_2)_6^{3+}$, one is encouraged, perhaps naively, to extend this to the cobalt(III) oxidants. If the E° for $\text{C}_6\text{H}_5\text{CH}_2^+$ is $\sim 0.7 \text{ V}$, a value consistent with the reactivity and pathway changeover with $\text{Fe}(\text{OH}_2)_6^{3+}$, then no set of self-exchange rate constants and E° values for the $(\text{NH}_3)_5\text{CoX}^{2+}$ complexes will predict the reduction rate constants with $\text{Ru}(\text{NH}_3)_6^{2+}$ and the values with the benzyl radical. The essential problem is that the E° difference of the reductants (0.051 vs 0.7 V) gives $\sim 10^{11}$ times smaller K_{12} for the radicals, which cannot be compensated by a radical self-exchange rate constant of 1×10^9 compared to $6.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ³⁴ for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$. Therefore the predicted radical reduction rate constants are $\sim 10^3$ times smaller than the values³⁵ with $\text{Ru}(\text{NH}_3)_6^{2+}$, which are 2.6×10^2 and $1.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for $(\text{NH}_3)_5\text{CoCl}^{2+}$ and $(\text{NH}_3)_5\text{CoBr}^{2+}$, respectively.

In summary, it is apparent that the wide range of oxidizability of the substituted benzyl radicals presents some interesting possibilities for measuring their

reactivity with different oxidizing agents. As yet it is unclear whether these rates will conform to Marcus theory, as seems to be the case with $\text{Fe}(\text{OH}_2)_6^{3+}$, or if there are special factors affecting the reactivity as for the halopentaaminecobalt(III) complexes.

Experimental Section

Materials. Solutions of the benzyl complexes of pentaquachromium(III) were prepared by mixing 2 mmol of the appropriate benzyl bromide (Aldrich) in 40 mL of methanol with 20 mL of aqueous 0.30 M chromium(II) perchlorate, prepared by reduction of chromium(III) perchlorate over amalgamated zinc. Each product complex was separated by ion exchange chromatography as described in Chapter 2, where the electronic spectra are also given.

Aqueous iron(III) perchlorate was prepared from iron wire as described by Xu and Jordan.³⁶ The $[(\text{NH}_3)_5\text{CoCl}](\text{ClO}_4)_2$ and $[(\text{NH}_3)_5\text{CoBr}](\text{ClO}_4)_2$ were prepared from $[(\text{NH}_3)_5\text{CoCl}](\text{Cl})_2$ ³⁷ and $[(\text{NH}_3)_5\text{CoBr}](\text{Br})_2$ ³⁸ by dissolving either 2 g of chloride or 1 g of bromide in 100 mL of 3.0 M NaClO_4 in 0.1 M HClO_4 at 50 °C, filtering the solution and cooling in an ice bath. The needles were collected by filtration, washed three times with cold methanol and twice with diethyl ether. The product was dried for 2 h at 45 °C. The absorbance maxima were found at $\lambda = 530$ nm (ϵ , 53 $\text{M}^{-1} \text{cm}^{-1}$), 362 (ϵ , 51) and 228 (ϵ , 1.71×10^4) for $[(\text{NH}_3)_5\text{CoCl}](\text{ClO}_4)_2$ and 548 (ϵ , 54), 252 (ϵ , 1.68×10^4) for $[(\text{NH}_3)_5\text{CoBr}](\text{ClO}_4)_2$.

Kinetic Measurements. The absorbance decrease was followed on a Hewlett Packard 8451 diode array spectrophotometer at an appropriate wavelength in the 310–360 nm region. The absorbance-time data (80 points over 5 to 6 half-lives) were analysed by least-squares to obtain the first-order rate constants. As noted in the discussion, some systems with dioxygen as the scavenger showed biphasic behavior

and were followed at 4 wavelengths. These data were fitted simultaneously to a biphasic model to obtain the two first-order rate constants.

Solutions for kinetic runs were prepared by adding the required amounts of standardized sodium perchlorate, perchloric acid and scavenger to a 50 mm cylindrical spectrophotometer cell. For scavengers other than dioxygen, the cell was closed with a serum cap, deoxygenated with argon purified by passing it through Cr(II) solution, brought to the required temperature and then enough of the benzylchromium(III) complex solution was added by syringe to give a chromium concentration of $\sim 2 \times 10^{-5}$ M. With dioxygen as the scavenger, the reaction was simply open to the air.

Product Analysis. Solutions of 0.12 to 0.2 mmol ($(1.8\text{--}3.2) \times 10^{-3}$ M) of the benzylchromium(III) complex in 0.1 M HClO_4 were prepared as for the kinetic runs. After stirring for about 4 h, the solution was extracted with 10 mL of chloroform. The solvent was evaporated, the extract redissolved in CDCl_3 and the ^1H NMR spectrum recorded on a Bruker AM 300 spectrometer. When appropriate, the aqueous phase was analysed for iron(II) or cobalt(II). The iron(II) produced was determined by titration with standardized potassium dichromate. The cobalt(II) was determined spectrophotometrically as $\text{Co}(\text{SCN})_4^{2-}$ in aqueous acetone by the method of Kitson.³⁹

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- based on the correlation found by Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *22*, 2557.
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Chapter 4. Kinetics of Heterolysis and Homolysis of Benzyl and Cyanobenzyl Complexes of Pentaquachromium(III) in Acetate Buffers*

Introduction

Organometallic complexes of pentaquachromium(III) are known¹ to undergo Cr–C bond breaking in aqueous solution by either heterolysis (k_{het}) or homolysis (k_{homo}). Since $\text{Cr}_{\text{aq}}^{2+}$ suppresses the homolysis reaction, the heterolysis can be studied by adding $\text{Cr}_{\text{aq}}^{2+}$ to the system. The heterolysis reaction typically shows pathways which are independent and first order in $[\text{H}^+]$. The homolysis can be promoted by the addition of scavengers for either Cr(II) or ($\text{R}^\bullet$), and then the observed decomposition is a mixture of heterolysis and homolysis ($k_{\text{obsd}} = k_{\text{het}} + k_{\text{homo}}$). The kinetics of the latter can be determined by difference from the two sets of conditions. In general, homolysis should be much faster than heterolysis so that the difference between k_{obsd} and k_{het} is large and an accurate value of k_{homo} can be obtained.

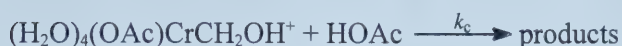
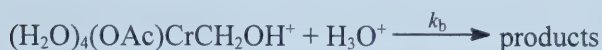
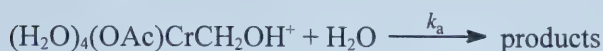
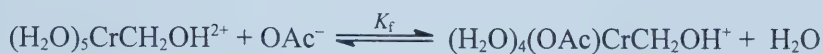
It was reported by Kochi and Buchanan² that acetate/acetic acid buffers effectively catalyse these decomposition reactions for the benzyl complex, $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5]^{2+}$ in ethanol-water mixtures. This study was done anaerobically, but without added scavengers for radicals (except possibly ethanol) or Cr(II). Recent work³ has shown that homolysis has a larger rate constant than heterolysis for this system, so that Kochi and Buchanan were probably observing homolysis initially but heterolysis in the later stages of the reaction as Cr(II) built up and suppressed homolysis. This

* A version of this chapter has been published. (a) Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1993**, 32, 2010–2012. (b) *Ibid.* **1993**, 32, 3412–3417.

accounts for the mixture of products (toluene from heterolysis, bibenzyl from homolysis) that was observed.

Ogino et al.⁴ studied the acetate/acetic acid dependence of the decomposition of $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}]^{2+}$ in aqueous buffers, and discussed the results in terms of the reaction pathways shown in Scheme I. The analysis gave $K_f = 11 \text{ M}^{-1}$, $k_a = 1.12 \text{ s}^{-1}$,

Scheme I



$k_b < 2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, and $k_c = 0.6 \text{ M}^{-1} \text{ s}^{-1}$. The k_b path could not be characterized, presumably because of the small $[\text{H}_3\text{O}^+]$ in the pH range 3.5 to 4.5 of the study.

In a series of papers, Cohen and co-workers⁵ further explored the heterolysis of $[\text{Cr}-\text{C}(\text{CH}_3)_n(\text{H})_{2-n}\text{OH}]^{2+}$ systems and the effect of nonreacting ligands such as acetate, nta and $[\text{15}] \text{aneN}_4$ on the reaction kinetics and volumes of activation. In the most recent study^{5c} of $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}]^{2+}$, Cohen et al. found $K_f = 26 \text{ M}^{-1}$ and $k_a = 0.94 \text{ s}^{-1}$, with $\Delta V^\circ(K_f) \approx 6$ and $\Delta V^*(k_a) \approx 8 \text{ cm}^3 \text{ mol}^{-1}$. The latter value was taken as indicative of dissociative activation for the heterolysis reaction, however subsequent discussion here indicates that this reaction may be proceeding by a mechanistically different, but kinetically equivalent pathway.

The present study is an investigation of the effect of acetate/acetic acid buffers on both the heterolysis and homolysis of the benzyl and the substituted benzyl

complexes, $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2+}$ ($\text{X} = \text{H}, 2\text{-CN}, 3\text{-CN}, 4\text{-CN}$). This system differs from $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}]^{2+}$ in that homolysis is the dominant process³ in the absence of Cr(II), so that the effect of acetate on both decomposition modes can be studied. For applications of these systems to generate aqueous organic radicals, it would be very useful if the homolysis could be controlled by the addition of complexing ions. The earlier work of Kochi and Buchanan² suffers from the uncertain mixture of heterolysis and homolysis that was being observed.

Results and Analysis

The decomposition of $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2+}$ ($\text{X} = \text{H}, 2\text{-CN}, 3\text{-CN}, 4\text{-CN}$) was monitored spectrophotometrically in aqueous solutions containing varying amounts of total acetate, at pH 3.0–5.0 and 1.0 M ionic strength ($\text{NaOAc}/\text{NaClO}_4$) at 25.0°C. The heterolysis reaction was studied under an argon atmosphere with solutions containing 2×10^{-3} M $\text{Cr}_{\text{aq}}^{2+}$ to suppress homolysis. The combination of homolysis and heterolysis was studied using O_2 from air as a scavenger for $\text{Cr}_{\text{aq}}^{2+}$ and radicals produced. The homolysis rate constants were determined by difference from the two types of studies, for runs under the same acetate and pH conditions. The results are summarized in Appendixes 4.1–4.8.

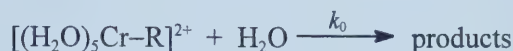
Heterolysis in Aqueous Acetate-Acetic Acid. The heterolysis data were analysed initially in terms of the reactions in Scheme I, which predict that the pseudo-first-order rate constant will be given by eq 4.1 where $[\text{OAc}^-]$ represents the acetate ion concentration, K_a is the mixed acid dissociation constant of acetic acid (1.9×10^{-5}

$$k_{\text{het}} = \frac{1}{K_f[\text{OAc}^-] + 1} \left\{ k_a K_f [\text{OAc}^-] + k_b K_f [\text{H}^+] [\text{OAc}^-] + \frac{k_c K_f [\text{H}^+] [\text{OAc}^-]^2}{K_a} \right\} \quad (4.1)$$

M),⁶ and $[H^+] = 10^{-pH}$. From the observations of Ogino et al.,⁴ one might expect the k_b term to be negligible at pH 3.0–5.0, so that eq 4.1 can be simplified to eq 4.2.

$$k_{het} = \frac{1}{K_f[OAc^-] + 1} \left\{ k_a K_f [OAc^-] + \frac{k_c K_f [H^+] [OAc^-]^2}{K_a} \right\} \quad (4.2)$$

However, from the previous studies of the heterolysis in the absence of acetate and in 0.01–0.90 M $HClO_4$ in Chapter 2, the following reaction should be considered,



especially for the 4-CN and 2-CN systems which have relatively larger k_0 values. Therefore, eq 4.2 is modified to eq 4.3. The kinetic results are fitted by least-squares

$$k_{het} = \frac{1}{K_f[OAc^-] + 1} \left\{ k_0 + k_a K_f [OAc^-] + \frac{k_c K_f [H^+] [OAc^-]^2}{K_a} \right\} \quad (4.3)$$

analysis of k_{het} to eq 4.3 and summarized in Table 4.1. A plot of k_{het} vs. $[OAc^-]$ is shown in Figure 4.1. Rearrangement of eq 4.3 gives eq 4.4. A plot of the left hand side

$$\frac{k_{het}(K_f[OAc^-] + 1) - k_0}{[OAc^-]} = \left\{ k_a K_f + \frac{k_c K_f [H^+] [OAc^-]}{K_a} \right\} \quad (4.4)$$

of eq 4.4 versus $[H^+][OAc^-]$ is shown in Figure 4.2 and Figure 4.3, for the data of Ogino et al.,⁴ and for our data, respectively. Clearly this model gives a good fit of the data. It is also apparent that the systems are different in that the plots for the

Table 4.1. Kinetic Parameters for the Heterolysis of Benzylpentaquachromium(III) Complexes in Acetate/Acetic Acid Buffers

benzyl substituent	K_f M^{-1}	$10^6 k_0$ s^{-1}	$10^4 k_a$ s^{-1}	$10^3 k_a'$ ^a $M^{-1} s^{-1}$	$10^3 k_c$ $M^{-1} s^{-1}$
H	65 ± 6	3.2	0.67	4.4	19
2-CN	128 ± 7	15	0.95	12.2	0.69
3-CN	107 ± 5	0.97	0.39	4.2	6.4
4-CN	127 ± 7	64	0.57	7.2	3.7

^a There is a kinetic ambiguity between k_a and k_a' as discussed in the text.

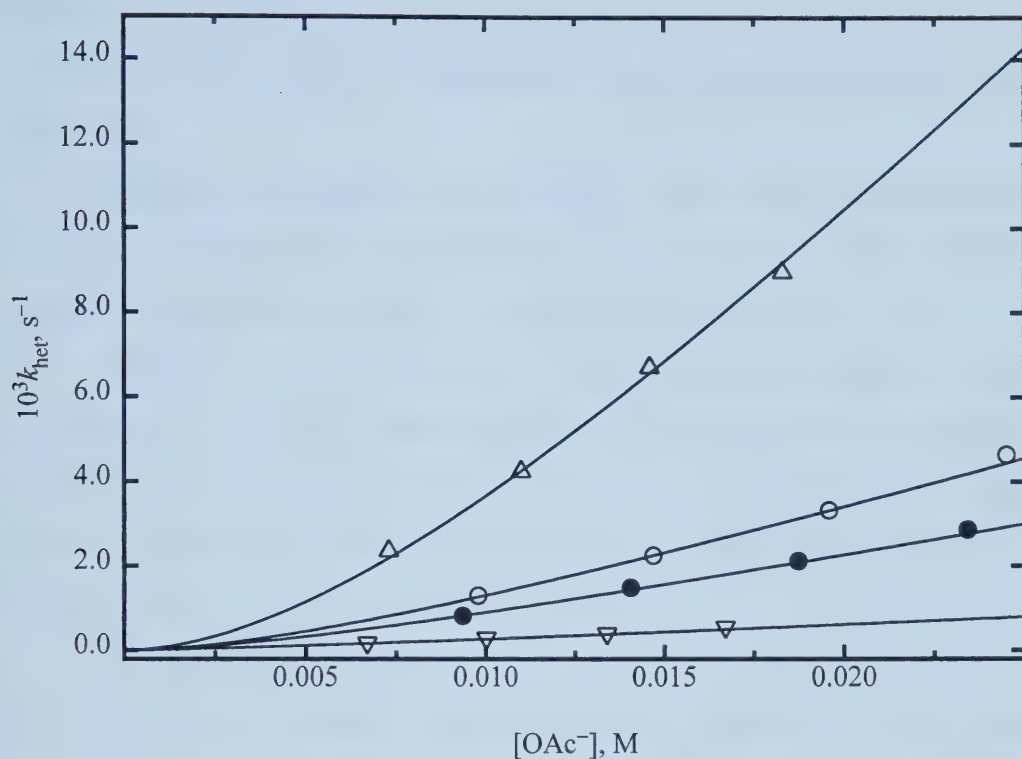


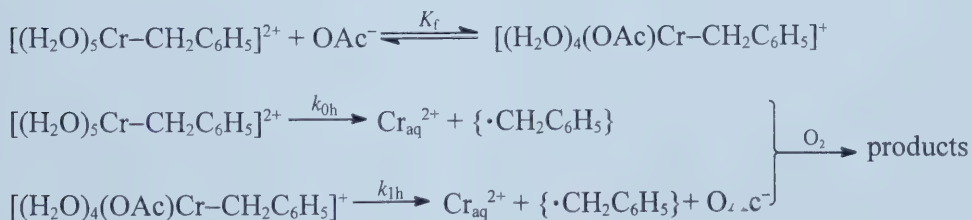
Figure 4.1. Variation of the rate constant for heterolysis with acetate ion concentration for the complexes of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}-$ with benzyl (Δ pH 3.01), 3-cyanobenzyl ($\circ$ pH 3.13), 4-cyanobenzyl ($\bullet$ pH 3.11), and 2-cyanobenzyl (∇ pH 2.96) at 25 °C in 1.00 M NaOAc/NaClO₄.

$[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2+}$ systems have only a marginally perceptible intercept, as shown by the inset on Figure 4.3, implying that the k_a path makes at most a small contribution.

Homolysis in Aqueous Acetate-Acetic Acid. Under aerobic conditions in the absence of acetate, the homolysis reaction⁶ ($k_{\text{homo}} = 2 \times 10^{-3}$ and $0.2 \times 10^{-3} \text{ s}^{-1}$) for the benzyl and 3-cyanobenzyl complexes is faster than the heterolysis³ ($k_{\text{het}} = 0.32 \times 10^{-5} + 1.7 \times 10^{-5}[\text{H}^+]$ and $0.12 \times 10^{-5} + 0.25 \times 10^{-5}[\text{H}^+]$, respectively). However, acetate accelerates the rate of heterolysis to the extent that heterolysis makes a significant contribution under homolysis (aerobic) conditions. As a result, the processes become kinetically competitive and the determination of k_{homo} is less accurate because it is obtained from the often small difference $k_{\text{obsd}} - k_{\text{het}}$.

The homolysis contribution to the experimental rate constant has been analysed in terms of Scheme II. The total observed rate constant is predicted to be given by eq 4.5, where k_{het} and K_f have been evaluated from the heterolysis kinetics described above, and k_{0h} was determined from studies in the absence of acetate⁷ and in 0.01–0.90 M HClO_4 in Chapter 3, k_{1h} is the only unknown in eq 4.5 and can be determined by least-squares fitting of k_{obsd} to eq 4.5.

Scheme II



$$k_{\text{obsd}} = k_{\text{het}} + \frac{k_{0h} + k_{1h}K_f[\text{OAc}^-]}{K_f[\text{OAc}^-] + 1} \quad (4.5)$$

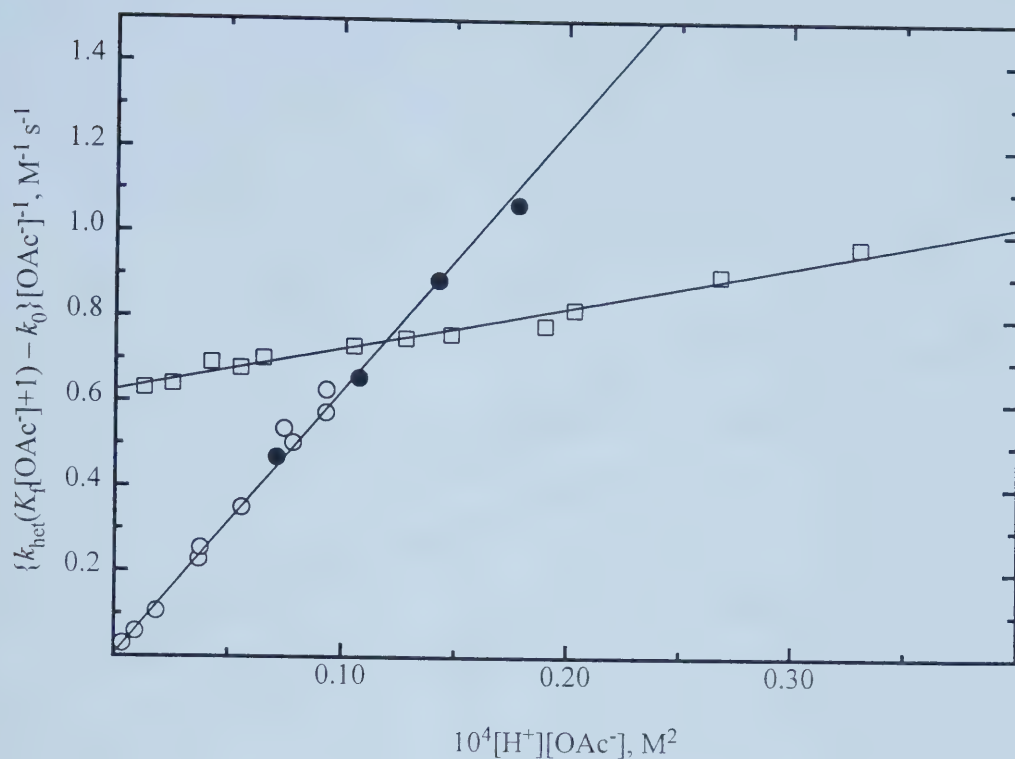


Figure 4.2. Variation of $\{k_{het}(K_f[OAc^-] + 1) - k_0\}[OAc^-]^{-1}$ with $[H^+][OAc^-]$ as predicted by eq 4.4 for the heterolysis of the complexes of $[(H_2O)_5Cr-CH_2C_6H_5]^{2+}$ ($\circ$ pH 4.5–5.0; $\bullet$ pH 3.01) and $[(H_2O)_5Cr-CH_2OH]^{2+}$ ($\square$ pH 3.5–4.5; ordinate values divided by 20; data from ref 4).

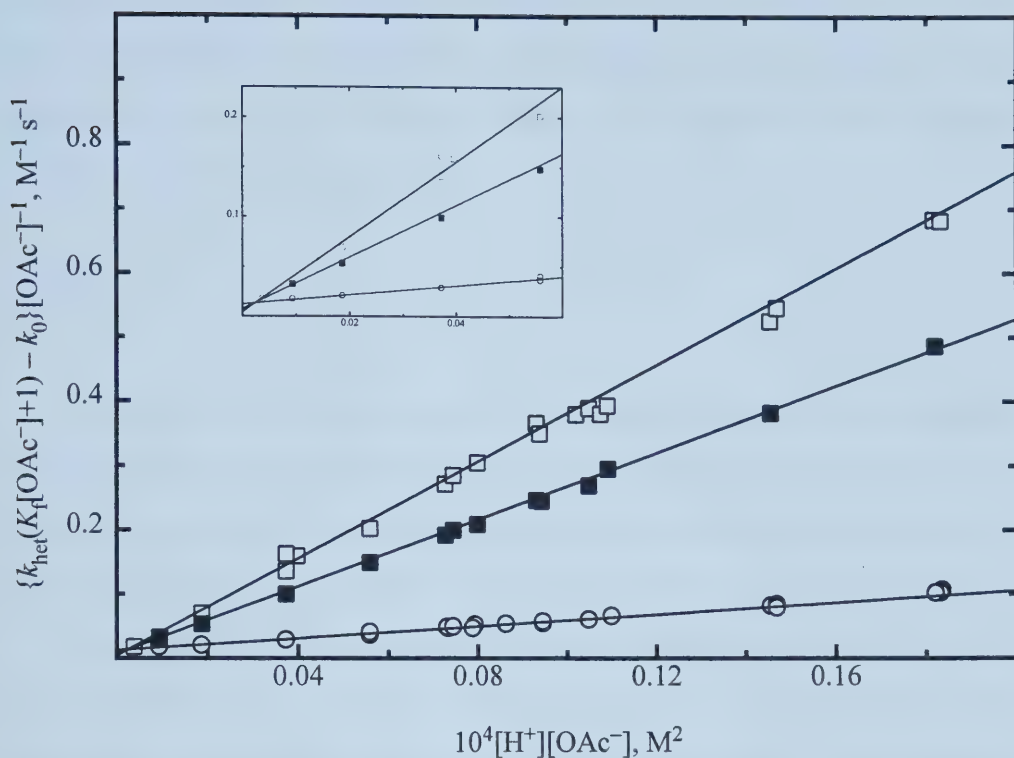


Figure 4.3. Variation of $\{k_{\text{het}}(K_f[\text{OAc}^-] + 1) - k_0\}[\text{OAc}^-]^{-1}$ with $[\text{H}^+][\text{OAc}^-]$ as predicted by eq 4.4 for the heterolysis of the complexes of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ – with 3-cyanobenzyl ($\square$), 4-cyanobenzyl ($\blacksquare$) and 2-cyanobenzyl ($\circ$) at 25 °C in 1.00 M NaOAc/NaClO₄.

The experimental conditions and observed and calculated values of k_{obsd} are given in Appendixes 4.5–4.8. The values of k_{oh} , and k_{lh} are given in Table 4.2. The experimental results for the benzyl complex are compared to the calculated dependence on $[\text{OAc}^-]$ in Figure 4.4.

Discussion

Since the effect of acetate complexing on homolysis had not been investigated previously, a significant new observation as given in Table 4.2 is that this effect is a rather minor enhancement on the homolysis rate constant for the benzyl, 3-CN and 4-CN substituted systems, but acetate provides a slight inhibition for the 2-CN system.

Our results for the heterolysis are qualitatively similar to the observations of Kochi and Buchanan² in that the rate increases with increasing acetic acid concentration. The different conditions (35 vol % ethanol-water, variable LiOAc–LiCl, 28.3 °C) make quantitative comparisons difficult, but one run (ref 2, Table 4.2, 0.55 M HOAc, pH 3.00, $k = 1.78 \times 10^{-2} \text{ s}^{-1}$.) has a rate constant ~ 4 times larger than the sixth run in Appendix 4.1 at similar pH and HOAc conditions.

The results of this and related work for the heterolysis are summarized in Table 4.3. A comparison of the heterolysis pathways $\text{H}_3\text{O}^+ + (\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ (k_{H}) and $\text{HOAc} + (\text{OAc})(\text{H}_2\text{O})_4\text{Cr-R}^+$ (k_{c}) for $\text{R} = \text{CH}_2\text{OH}$,⁴ $\text{CH}_2\text{C}_6\text{H}_5$ and $3\text{-CNC}_6\text{H}_4\text{CH}_2$ reveals that the HOAc reaction is close to $(1.2\text{--}2.2) \times 10^3$ times more effective in these systems. However, the H_2O pathways (k_{a} and k_{w}) in these systems reveal no such consistency. For $\text{R} = \text{CH}_2\text{OH}$, the pathway involving acetate ion has a 1.7×10^3 times larger rate constant, whereas this factor is only 21 and 16 for $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ and $3\text{-CNC}_6\text{H}_4\text{CH}_2$, respectively. This leads one to question whether the $-\text{OH}$ function is such an innocent

Table 4.2. Kinetic Parameters for the Homolysis of Benzylpentaquachromium(III) Complexes in Acetate/Acetic Acid Buffers

benzyl substituent	$10^4 k_{\text{oh}}, \text{ s}^{-1}$	$(k_{1\text{h}}' + k_{1\text{h}}K_{\text{f}}), \text{ M}^{-1} \text{ s}^{-1}$	
		$10^4 k_{1\text{h}}^a$	$k_{1\text{h}}'^a$
H	20	36 ± 0.8	0.23 ± 0.008
2-CN	3.8	3.0 ± 0.05	0.038 ± 0.0007
3-CN	2.1	5.5 ± 0.14	0.059 ± 0.0015
4-CN	3.4	5.2 ± 0.12	0.066 ± 0.0016

^a This value is not defined by the data and has been assumed for reasons described in the text.

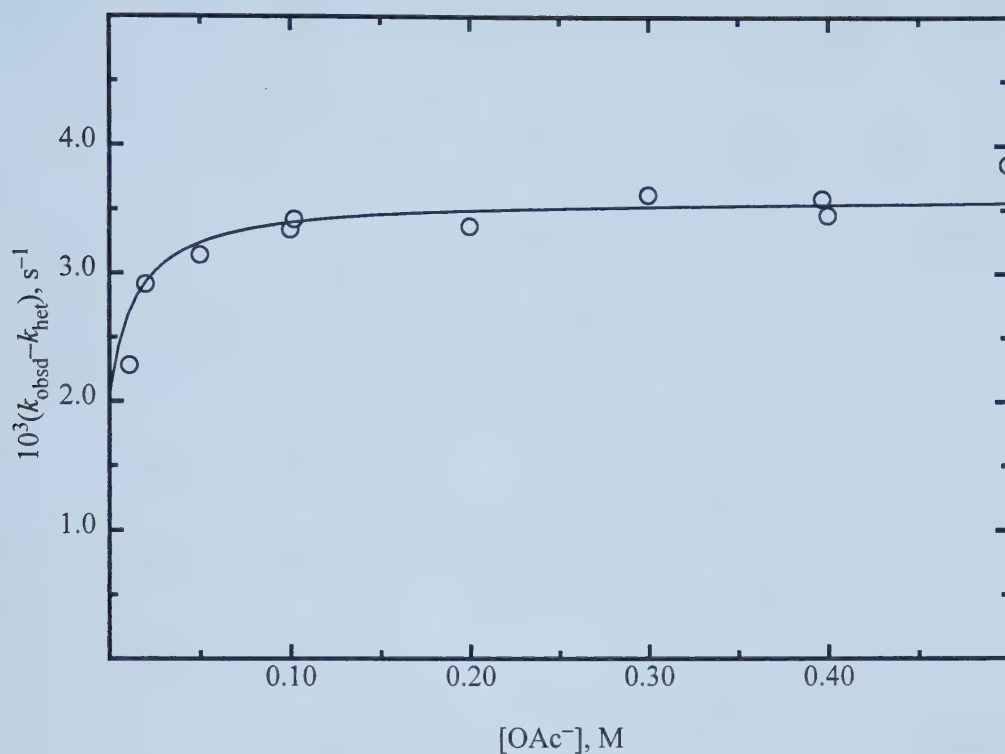


Figure 4.4. Variation of the rate constant for homolysis of $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5]^{2+}$ with acetate ion concentration. The curve is calculated on the basis of a least-squares fit to eq 4.5.

Table 4.3. Summary of Rate Constants at 25°C for Heterolysis of $[(\text{H}_2\text{O})_5\text{Cr-R}]^{2+}$ Systems

Reaction		R		
		$\text{CH}_2\text{C}_6\text{H}_5^a$	$3\text{-CNC}_6\text{H}_4\text{CH}_2^a$	CH_2OH^b
$[(\text{H}_2\text{O})_5\text{Cr-R}]^{2+} + \text{H}_2\text{O}$	k_w, s^{-1}	$3.3 \times 10^{-6}{}^c$	$0.97 \times 10^{-6}{}^c$	6.6×10^{-4}
$[(\text{H}_2\text{O})_5\text{Cr-R}]^{2+} + \text{H}_3\text{O}^+$	$k_H, \text{M}^{-1} \text{s}^{-1}$	$1.7 \times 10^{-5}{}^c$	$2.5 \times 10^{-6}{}^c$	4.65×10^{-4}
$[(\text{OAc})(\text{H}_2\text{O})_4\text{Cr-R}]^+ + \text{H}_2\text{O}^d$	k_a, s^{-1}	6.9×10^{-5}	3.9×10^{-5}	$1.1^e (0.95)^f$
$[(\text{H}_2\text{O})_5\text{Cr-R}]^{2+} + \text{OAc}^-^d$	$k_a', \text{M}^{-1} \text{s}^{-1}$	4.5×10^{-3}	4.2×10^{-3}	$12.1^e (24.7)^f$
$[(\text{OAc})(\text{H}_2\text{O})_4\text{Cr-R}]^+ + \text{HOAc}$	$k_c, \text{M}^{-1} \text{s}^{-1}$	1.9×10^{-2}	6.4×10^{-3}	0.6^e

^aThis work in 1.0 M NaClO_4 . ^b Values from ref. 1 unless otherwise indicated. ^c Values from Chapter 2. ^d There is a kinetic ambiguity between k_a and k_a' as discussed in the text. ^e Taken from ref. 4 in 1 M LiClO_4 . ^f Taken from ref. 5c in 0.5 M NaClO_4 .

bystander for the reaction involving acetate ion, or whether the kinetics have been properly interpreted.

It is known¹ that changing from $R = \text{CH}_2\text{OCH}_3$ to CH_2OH increases the heterolysis rate constant from $<10^{-6}$ to $6.6 \times 10^{-4} \text{ s}^{-1}$, and such effects have been attributed^{5a,8} to stabilization of the transition state through hydrogen bonding of the $-\text{OH}$ to *cis*-ligands on chromium. Complexation by acetate would enhance this effect by making the *cis*- H_2O ligands more basic, but it is not clear that the further rate enhancement would be so large. A comparison of *cis*- $[(\text{nta})(\text{H}_2\text{O})\text{Cr}-\text{R}]^{-5c}$ and $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes⁸ ($R = \text{CH}_2\text{OH}$, $\text{CH}(\text{CH}_3)\text{OH}$ and $\text{C}(\text{CH}_3)_2\text{OH}$), reveals that heterolysis is affected by modest factors of <5 . Therefore, it seems surprising that a single coordinated acetate would increase the heterolysis rate constant by a factor of 1.7×10^3 in the $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{OH}^{2+}$ system.

It has not been previously recognized that the k_a path in Scheme I is kinetically equivalent to reaction 4.6, in which acetate ion is reacting with the uncomplexed



chromium complex. Then eq 4.3 must be modified by the addition of the term $k_a'[\text{OAc}^-]/(K_f[\text{OAc}^-] + 1)$ to become eq 4.7. Since the rate for reaction 4.6 is

$$k_{\text{het}} = \frac{1}{K_f[\text{OAc}^-] + 1} \left\{ k_0 + (k_a' + k_a K_f)[\text{OAc}^-] + \frac{k_c K_f [\text{H}^+][\text{OAc}^-]^2}{K_a} \right\} \quad (4.7)$$

$k_a' \{[(\text{H}_2\text{O})_5\text{Cr}-\text{R}]^{2+}\}[\text{OAc}^-]$ which is equal to $k_a K_f \{[(\text{H}_2\text{O})_5\text{Cr}-\text{R}]^{2+}\}[\text{OAc}^-]$, there is a kinetic ambiguity between k_a' and $k_a K_f$. If this term is assigned exclusively to k_a' , then one obtains values of 4.4×10^{-3} , 4.2×10^{-3} , 12, 140 and $210 \text{ M}^{-1} \text{ s}^{-1}$ for $R = \text{CH}_2\text{C}_6\text{H}_5$, 3-CNC₆H₄CH₂, CH_2OH , $\text{CH}(\text{CH}_3)\text{OH}$ and $\text{C}(\text{CH}_3)_2\text{OH}$, respectively, and the ratios of

k_a' to k_w are 1.3×10^3 , 4.3×10^3 , 1.8×10^4 , 7.4×10^4 and $6.4 \times 10^4 \text{ M}^{-1}$, respectively. This analysis implies that the acetate catalysis is somewhat enhanced by an α -OH on the alkyl group, but by a factor of 10–40 rather than 1.7×10^3 as required by the k_a pathway assignment. The k_a' reaction might proceed by a conjugate base mechanism, with acetate ion acting as a base towards a coordinated water ligand. This pathway might be enhanced by hydrogen bonding of the conjugate base and the α -OH. For the *cis*-[(nta)(H₂O)Cr-R]⁻ systems,^{5a} the k_a' to k_w ratio drops to $\sim 10^2$, which is consistent with the expected lower acidity of the *cis*-H₂O in the nta complexes.

The above assumption that $k_a' \gg k_a K_f$ is not necessarily universally true, but it is suggested to be reasonably valid for acetate, and bases of similar basicity. The mechanistic suggestion involving eq 4.6 predicts that other bases should catalyse the heterolysis of these complexes, and that the magnitude of this catalysis should correlate with the pK_a of the conjugate acid of the base until the basicity drops to a level where the $k_a K_f$ becomes significant or dominant. This prediction is consistent with the recent results on the anion-catalysed heterolysis reaction of [(H₂O)₅Cr-C(CH₂)₃OH]²⁺, in that the rate of the catalysed heterolysis reaction increases with increasing pK_a value of the anions.⁹

Finally, the effect of acetate ion on the homolysis reaction will be discussed. Like heterolysis there is a kinetic ambiguity between the paths involving (OAc)(H₂O)₄Cr-R⁺ + H₂O (k_{1h}) and (H₂O)₅Cr-R²⁺ + OAc⁻ (k_{1h}'), so that eq 4.5 is modified to eq 4.8. Since the kinetic effect of acetate ion is small, most of the runs were done at high [OAc⁻] so that $K_f[\text{OAc}^-] > 1$ in eq 4.8. Therefore, most of the data are in the saturation region where the expression $(k_{1h}' + k_{1h}K_f)[\text{OAc}^-]/(K_f[\text{OAc}^-] + 1)$

$$k_{\text{obsd}} = k_{\text{het}} + \frac{k_{0h} + (k_{1h}' + k_{1h}K_f)[\text{OAc}^-]}{K_f[\text{OAc}^-] + 1} \quad (4.8)$$

gives the value of k_{1h}/K_f or k_{1h} , depending on the assignment. These values are given in Table 4.2. For the benzyl, 3-CN, and 4-CN systems k_{1h} is 1.5–2.5 times larger than k_{0h} , but for the 2-CN system the value is actually smaller than k_{0h} . Espenson et al.¹⁰ observed that the *trans*-OH⁻ in several $[(15)\text{aneN}_4](\text{OH})\text{Cr}-\text{R}^+$ complexes strongly suppresses homolysis and favors heterolysis relative to the *trans*-OH₂ system. This would appear to be due to stabilization of the Cr(III) oxidation state relative to Cr(II) by the *trans* ligand. A similar effect might be expected for acetate ion, so that one could expect k_{1h} to be smaller than k_{0h} . The relative balance of k_{1h} and k_{1h}' will determine whether one finds an increased or decreased rate of homolysis with increasing concentrations of acetate ion. This does not permit a separation of k_{1h} and k_{1h}' , but it does provide a rationalization for the reactivity difference of the 2-CN system. It may be that the k_{1h}' pathway is inhibited by the 2-CN substituent by the same steric and electronic factors suggested for heterolysis by the k_c pathway. Then the k_{1h} contribution may dominate and cause the inhibition to homolysis observed for the 2-CN complex.

Experimental Section

Materials. Aqueous solutions of $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2+}$ were prepared by mixing 40 mL of deoxygenated methanol containing 2 mmol of the appropriate benzyl bromide with 20 mL of aqueous 0.3 M chromium(II) perchlorate, prepared by amalgamated zinc reduction of aqueous chromium(III) perchlorate. After ~10 min at ambient temperature the solution had changed from pale blue to dark greenish yellow, and was loaded onto a column (8 × 2 cm) of Dowex 50W-X2(200) ion exchange resin in either the H⁺ or Na⁺ form under an argon atmosphere at 0 °C. Excess Cr(II) was

eluted with 0.6 M NaClO₄ in 0.01 M HClO₄, and the desired product was eluted with 1.0 M NaClO₄ in 0.01 M HClO₄. The product was stored at -10 to -15 °C.

The acetate/acetic acid buffers were prepared from solutions of sodium acetate trihydrate (BDH) by adding standardized perchloric acid to obtain the desired pH. The initial solutions contained enough sodium perchlorate to give a final ionic strength of 1.0 M. The uncertainty in the pH is ±0.002 units.

Kinetic Measurements. The absorbance decrease at 356 nm was followed on a Hewlett Packard 8451 diode array spectrophotometer equipped with a thermostated cylindrical cell holder and standard water circulating temperature control system. A 50 mm cylindrical quartz cell was used throughout. The data analysis typically involved 80 points over 5–6 half-lives which were analysed by nonlinear least-squares to a first-order model.

For the heterolysis reaction, 10 mL of acetate buffer and sodium perchlorate, to control ionic strength, were placed in the cell, sealed with serum caps and deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) perchlorate and [(H₂O)₅Cr-CH₂C₆H₄X]²⁺ to give final concentrations of 2 × 10⁻³ M and 1 × 10⁻⁴ M, respectively. For the homolysis, the chromium(II) was omitted and the reaction solution was exposed to air throughout the run.

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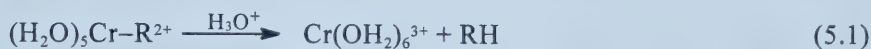
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Chapter 5. Kinetics of the Heterolysis of Benzyl and Cyanobenzyl Complexes of Pentaquachromium(III) in Phosphate Buffers*

Introduction

Pentaquachromium(III) forms a wide range of organometallic complexes,¹ $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$, which decompose in aqueous solution by either heterolysis (5.1) or homolysis (5.2). The heterolysis can be studied by adding $\text{Cr}_{\text{aq}}^{2+}$ to suppress



homolysis, while homolysis plus heterolysis can be observed if scavengers for $\text{Cr}_{\text{aq}}^{2+}$ or $\{\text{R}\cdot\}$ are added.

In Chapter 4,² we found that acetate increases the heterolysis rate for the $\text{R} = -\text{CH}_2\text{C}_6\text{H}_5$ system, but by much less than for the $\text{R} = -(\text{C}(\text{CH}_3)_n\text{H}_{2-n}\text{OH})$ systems examined earlier by Ogino et al.³ and Cohen and co-workers.⁴ These observations led to the suggestion that the α -OH function may not be an innocent bystander in the process, and to the recognition that there are possible kinetic ambiguities in the mechanistic interpretation of the results. We also observed that homolysis of the Cr-benzyl bond shows a modest enhancement in the presence of acetate.

The present study examines the heterolysis kinetics of benzyl and cyano substituted benzyl complexes in the presence of dihydrogen phosphate/hydrogen

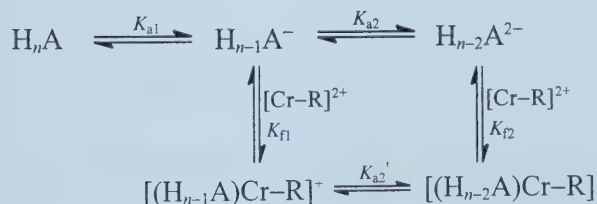
* A version of this chapter has been published. Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1993**, *32*, 3412–3417.

phosphate, methylhydrogenphosphate/methylphosphate for comparison with the previous results in the presence of acetate/acetic acid. It is hoped that an examination of systems with such diverse acidities will elucidate the mechanistic factors important for the assisted heterolysis of these systems, and may clarify the kinetic ambiguities inherent in the rate laws.

Results

Earlier studies²⁻⁴ have shown the general reactions which can be expected to describe the kinetic observations. Therefore, we will proceed directly to develop a general rate law and symbolism and then adapt them to the specific systems. The complexation equilibria of a general polybasic acid H_nA with $(H_2O)_5Cr-R^{2+}$ can be represented by Scheme I. It is known that these complexes undergo rather rapid replacement of the *trans* aqua ligand⁵⁻⁸ so that only formation of the mono complex is considered. There is the possibility of ion pairing as well as inner-sphere complex

Scheme I

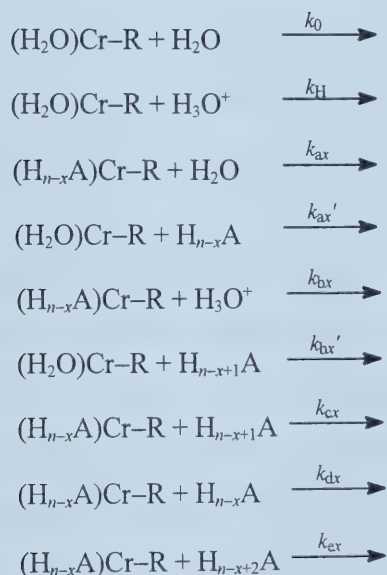


formation in these systems, although this is not formally included in Scheme I. The net formation constant (K_f) defined in Scheme I is actually the sum of the ion pair formation constant (K_i) and the inner-sphere complex formation constant (K_c). Scheme I has been simplified by neglecting the third ionization which gives $H_{n-3}A^{3-}$, because

the highest experimental pH of ~ 5 is much smaller than pK_{a3} of 12.3 of H_3PO_4 , so that PO_4^{3-} is never a significant species under our conditions.

On the basis of previous experience with these systems, the reaction pathways for heterolytic cleavage of the Cr–R bond can be represented in a general way by Scheme II. Only the organo ligand and the one *trans* to it are included in the scheme, and charges are omitted for generality. The k_0 and k_H pathways are observed in the absence of any complexing agents. The other pathways are grouped together according to the number of ionizable protons in the reactants and therefore will show the same

Scheme II



$[H^+]$ dependence in the final rate law expression. This may also be true for different pathways involving different $H_{n-x}A^{x-}$ species, and it is apparent that there are a number of possibilities for the so-called proton ambiguity to arise in such a system. In addition, there are kinetic ambiguities for reactions involving free or complexed $H_{n-x}A^{x-}$, since $(H_{n-x}A)Cr-R + H_2O$ is equivalent to $(H_2O)Cr-R + H_{n-x}A^{x-}$. Scheme II is not an

exhaustive list of the possibilities. Complexes $(H_nA)Cr-R$ are omitted on the assumption that the acid must lose at least one proton to form a complex. Reactions of $(H_{n-x+1}A)Cr-R + H_{n-x}A^{x-}$ are not included because the coordinated ligand is more acidic so that this combination would involve minor species and will have the same H^+ dependence as the k_{cx} path. In the formalism of Scheme II, k_{a1}' and k_{b2}' are the same and the latter is not included in the analysis.

If the reactions in Scheme I are treated as rapidly maintained equilibria, then the pseudo-first order rate constant ($[A]_{tot} \gg [Cr-R]_{tot}$) can be expressed as in eq 5.3, where $F_m = 1 + K_{f1}[H_{n-1}A] + K_{f2}[H_{n-2}A]$. The derivation of eq 5.3 and the following eq, 5.4, are shown in Appendix 5.1.

$$\begin{aligned}
 k_{obsd} = (F_m)^{-1} & (k_0 + k_H[H^+] + k_{a1}K_{f1}[H_{n-1}A] + k_{a1}'[H_{n-1}A] + k_{b1}K_{f1}[H^+][H_{n-1}A] + k_{b1}'[H_nA] \\
 & + k_{a2}K_{f2}[H_{n-2}A] + k_{a2}'[H_{n-2}A] + k_{b2}K_{f2}[H^+][H_{n-2}A] + k_{c1}K_{f1}[H_{n-1}A][H_nA] \\
 & + k_{c2}K_{f2}[H_{n-2}A][H_nA] + k_{c2}K_{f2}[H_{n-2}A][H_{n-1}A] + k_{d1}K_{f1}[H_{n-1}A]^2 + k_{d2}K_{f2}[H_{n-2}A]^2)
 \end{aligned} \quad (5.3)$$

In order to identify the distinguishable terms in eq 5.3, it is necessary to express the concentrations of the various conjugate base species in terms of the total concentration $[A]_{tot}$ ($= [H_nA] + [H_{n-1}A] + [H_{n-2}A] + [H_{n-3}A]$) and the acid dissociation constants of the acid, and then group terms according to their $[A]_{tot}$ and $[H^+]$ dependencies. If one assumes for generality a tribasic acid, then it is convenient to define $F_A = [A]_{tot}([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})^{-1}$. Substitution into eq 5.3 and rearrangement yields eq 5.4, where $k_1 = k_{a2}K_{f2} + k_{a2}'$, $k_2 = k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2}$, $k_3 = k_{b1}K_{f1}K_{a1} + k_{b1}'$, $k_4 = k_{d2}K_{f2}$, $k_5 = k_{c2}K_{f2}$, $k_6 = k_{d1}K_{f1}K_{a1} + k_{c2}K_{f2}K_{a2}$ and $k_7 = k_{c1}K_{f1}$.

$$\begin{aligned}
 k_{obsd} = (F_m)^{-1} & (k_0 + k_H[H^+] + F_A \{ k_1K_{a1}K_{a2}[H^+] + k_2K_{a1}[H^+]^2 + k_3[H^+]^3 + \\
 & F_A(k_4(K_{a1}K_{a2})^2[H^+]^2 + k_5K_{a1}^2K_{a2}[H^+]^3 + k_6K_{a1}[H^+]^4 + k_7K_{a1}[H^+]^5) \})
 \end{aligned} \quad (5.4)$$

Heterolysis in Aqueous Acetate-Acetic Acid. In Chapter 4, we have discussed the heterolysis of the benzyl and cyanobenzyl complexes in acetate/acetic acid buffers. Since acetate/acetic acid is a monobasic acid system, it is the simplest to analyse by eq 5.4 and provides some basic information for analysis of the polybasic acids. For acetate/acetic acid, all terms containing k_{i2} ($i = a; b; c; d$ and e) and K_{i2} are zero, and $F_A = [\text{OAc}^-]_{\text{tot}}[\text{H}^+]^{-2}(K_{a1} + [\text{H}^+])^{-1}$. Then eq 5.4 simplifies to eq 5.5 (see Appendix 5.1 for the derivation of eq 5.5). Qualitatively, the rate law predicts that a

$$k_{\text{obsd}} = \{1 + K_{f1}K_{a1}(K_{a1} + [\text{H}^+])^{-1}[\text{OAc}^-]_{\text{tot}}\}^{-1} \{k_0 + k_{\text{H}}[\text{H}^+] + \{k_2K_{a1} + k_3[\text{H}^+] + (k_6K_{a1}^2 + k_7K_{a1}[\text{H}^+])[\text{OAc}^-]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}\}([\text{OAc}^-]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1})\} \quad (5.5)$$

saturation effect may be observed when $K_{f1}K_{a1}(K_{a1} + [\text{H}^+])^{-1}[\text{OAc}^-]_{\text{tot}}$ becomes larger than 1, but this will be mitigated by the $[\text{OAc}^-]_{\text{tot}}$ squared dependence of the k_6 and k_7 terms. The $k_2 (=k_{a1}K_{f1} + k_{a1}')$ and $k_3 (=k_{b1}K_{f1}K_{a1} + k_{b1}')$ terms are distinguishable because of the $[\text{H}^+]$ dependence of the latter, but the proton ambiguity prevents distinction between k_{a1} and k_{a1}' or k_{b1} and k_{b1}' .

The kinetics of the heterolysis of the benzyl and cyanobenzyl systems have been studied between pH 3 and 5 with total acetate concentrations of 0.05 to 1.0 M in 1.0 M $\text{NaClO}_4/\text{NaOAc}$, at 25.0 °C. The kinetic behavior for those systems is similar. In all cases, it was possible to determine K_{f1} from the kinetic data, but only the k_2 and k_7 kinetic terms could be identified. Under these circumstances, eq 5.5 simplifies to eq 5.6, where $[\text{OAc}^-]$ is the acetate ion concentration ($= K_{a1}(K_{a1} + [\text{H}^+])^{-1}[\text{OAc}^-]_{\text{tot}}$). The form of eq 5.6 is the same as that of eq 4.7 in Chapter 4, in which $k_2 = k_{a1}' + k_{a1}K_f$ and $k_7 = k_{c1}K_f$.

$$k_{\text{obsd}} = \frac{1}{K_{f1}[\text{OAc}^-] + 1} \left\{ k_0 + k_2[\text{OAc}^-] + \frac{k_7[\text{H}^+][\text{OAc}^-]^2}{K_{a1}} \right\} \quad (5.6)$$

Heterolysis in Aqueous Hydrogen Phosphate/Dihydrogenphosphate. The presence of phosphate species in the pH 2–5 range substantially accelerates the rate of heterolysis of the benzyl systems. Since there are no previous studies of the total phosphate and hydrogen ion dependence of such reactions, these results will be presented more fully.

Since $K_{a3} \ll [H^+]$, the expression for F_A simplifies to $F_A = [PO_4]_{tot}[H^+]^{-1}([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})^{-1} = F_p[H^+]^{-1}$, and $F_m = 1 + (K_{f1}K_{a1}[H^+] + K_{f2}K_{a1}K_{a2})F_p$, where $[PO_4]_{tot} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}]$. Then k_{obsd} is given by eq 5.7.

$$k_{obsd} = (F_m)^{-1} \{ k_0 + k_H[H^+] + \{ k_1K_{a1}K_{a2} + k_2K_{a1}[H^+] + k_3[H^+]^2 + (k_4(K_{a1}K_{a2})^2 + k_5K_{a1}^2K_{a2}[H^+] + k_6K_{a1}^2[H^+]^2 + k_7K_{a1}[H^+]^3)F_p \} F_p \} \quad (5.7)$$

Typical results for the dependence of k_{obsd} on pH at constant $[PO_4]_{tot}$ and on $[PO_4]_{tot}$ at constant pH are shown in Figures 5.1 and 5.2, respectively. It is apparent from these plots that the reactivity order is benzyl > 3-CN > 4-CN > 2-CN, and that the rate increases with increasing pH for all these systems. Since the upper pH limit of this study is far below the pK_a of 7.2 of $H_2PO_4^-$, the pH dependence indicates that HPO_4^{2-} is very effective at promoting heterolysis. The incipient leveling (saturation) at high pH also implies strong complexation by HPO_4^{2-} . This is shown more clearly in Figure 5.3 for the benzyl system for rate constants at nearly constant pH and varying $[PO_4]_{tot}$.

Least-squares analysis of the variation of k_{obsd} with $[PO_4]_{tot}$ and $[H^+]$ reveals that K_{f1} and K_{f2} are defined for all the systems, that terms second order in $[PO_4]_{tot}$ (i.e. k_4 , k_5 , k_6 , k_7 in eq 5.7) are indeterminate as is the term k_3 second order in $[H^+]$. Therefore the kinetic terms that can be evaluated are $k_1 = (k_{a2}K_{f2} + k_{a2}')$ and $k_2 = (k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2})$. The best-fit parameters are summarized in Table 5.1 and the observed and

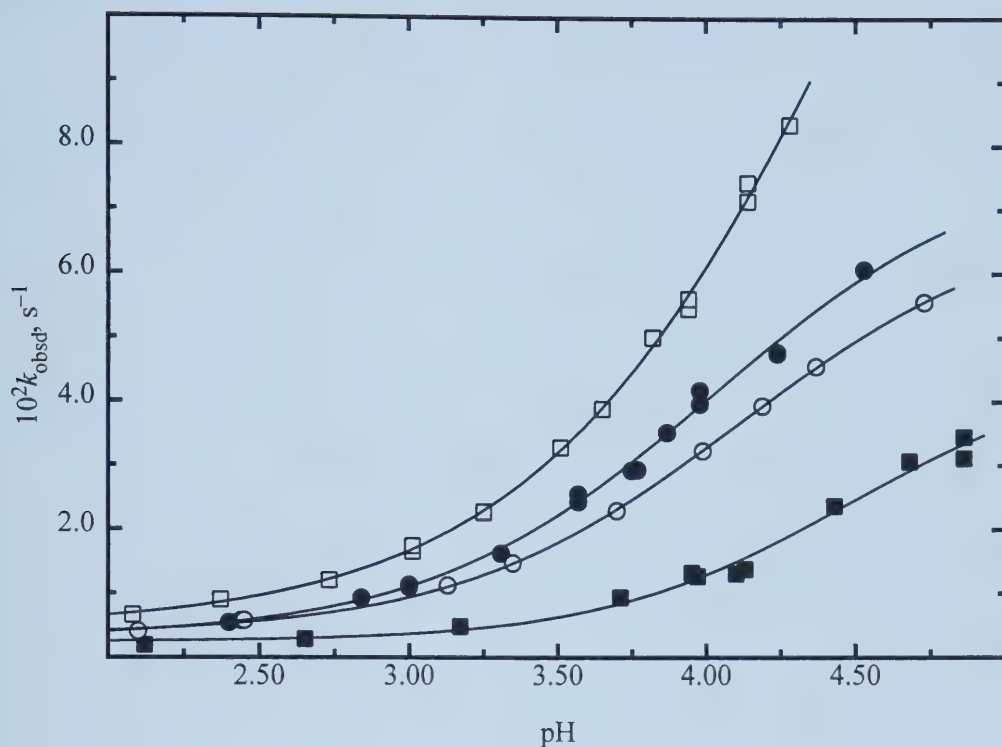


Figure 5.1. Variation of the rate constant for heterolysis in phosphate buffers with pH for the complexes of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ – with benzyl ($\square$), 0.30 M $[\text{PO}_4]_{\text{tot}}$; 3-cyanobenzyl ($\bullet$), 0.30 M $[\text{PO}_4]_{\text{tot}}$; 4-cyanobenzyl ($\circ$), 0.50 M $[\text{PO}_4]_{\text{tot}}$; and 2-cyanobenzyl ($\blacksquare$), 0.50 M $[\text{PO}_4]_{\text{tot}}$, at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$.

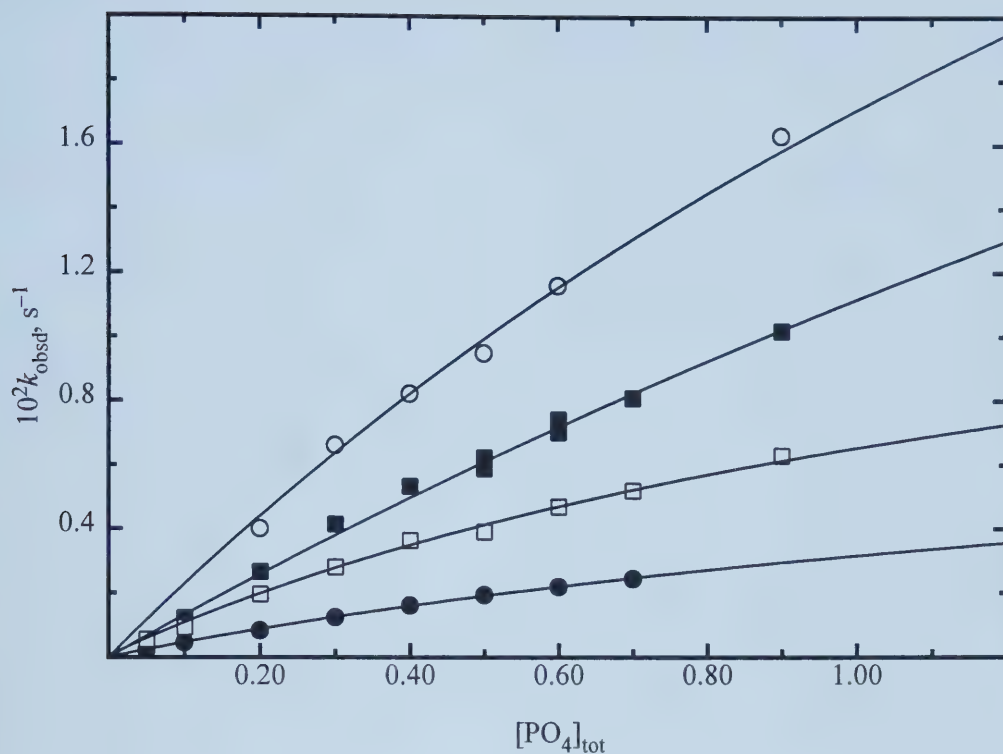


Figure 5.2. Variation of the rate constant for heterolysis in phosphate buffers with total phosphate concentration for the complexes of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}-$ with benzyl (○), pH 2.10; 3-cyanobenzyl (■), pH 2.11; 4-cyanobenzyl (□), pH 2.09; and 2-cyanobenzyl (●), pH 2.09, at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$.

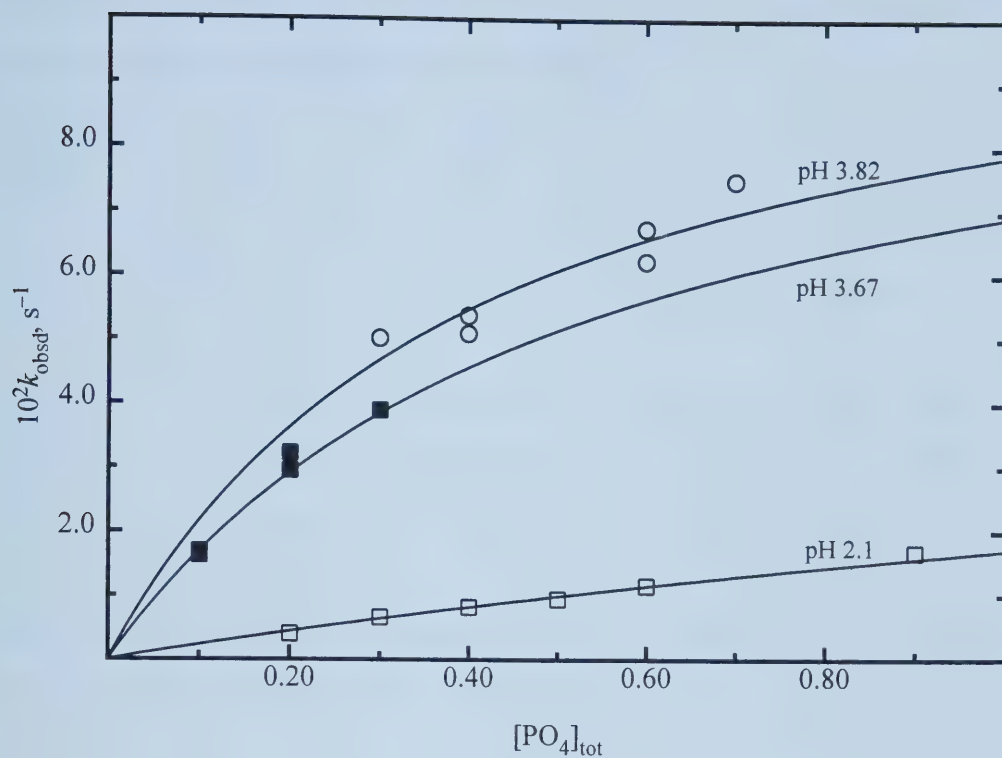


Figure 5.3. Variation of the rate constant for heterolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ in phosphate buffers with total phosphate concentration at several pH values and at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$.

Table 5.1. Kinetic Parameters for the Heterolysis of Benzylpentaquachromium(III) Complexes in Phosphate and Methylphosphate Buffers

Benzyl Substituent	$K_{f1},$ M^{-1}	$10^{-3}K_{f2},$ M^{-1}	$k_1,$ $M^{-1} s^{-1}$	$10^2k_2,$ $M^{-1} s^{-1}$
H	0.75 ± 0.19	4.21 ± 0.44	565 ± 24	4.4 ± 0.2
H ^a	$(0.2)^b$	0.55	2.7	0.1
2-CN	1.02 ± 0.14	1.42 ± 0.13	66.3 ± 3.3	0.92 ± 0.028
3-CN	0.37 ± 0.13	5.08 ± 0.30	417 ± 16	2.4 ± 0.009
4-CN	1.37 ± 0.13	4.03 ± 0.27	275 ± 13	2.05 ± 0.05

^a Results in monomethylphosphate buffers. ^b This value is not defined by the data and has been assumed for reasons described in the text.

calculated rate constants are given in Appendixes 5.2–5.6. The curves in Figure 5.1 to 5.3 are drawn with these parameters.

As noted in the introduction to this chapter, the K_f values are the sum of ion pair and inner-sphere complex formation constants, K_i and K_c , respectively. The magnitudes of the K_i can be estimated from previous work. Ferrer and Sykes⁹ found $K_i = 2 \text{ M}^{-1}$ (1.00 M LiClO_4 , 40 °C, $\Delta H^\circ \approx 0$) for $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+} + \text{H}_2\text{PO}_4^-$ and Boreham et al.¹⁰ obtained $K_i \approx 60 \text{ M}^{-1}$ (1.0 M NaClO_4 , 25 °C) for $(\text{H}_2\text{O})(\text{en})_2\text{Co}-(\text{NH}_2\text{CH}_2\text{CO}_2\text{C}_3\text{H}_7)^{3+} + \text{HPO}_4^{2-}$ or $\text{CH}_3\text{PO}_4^{2-}$. These should be upper limits for our system because of the lower charge of the $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes. Since our K_{f2} values are $>1.4 \times 10^3 \text{ M}^{-1}$ and K_i for HPO_4^{2-} is $< 60 \text{ M}^{-1}$, then the K_{f2} values are essentially identical to the inner-sphere complex formation constants. For K_{f1} , the situation is not so clear because the values are of the magnitude of 1 M^{-1} , while the K_i for H_2PO_4^- is $< 2 \text{ M}^{-1}$, and one must expect some ion pairing contribution to the K_{f1} values.

The acid dissociation constant (K_{a2}') for coordinated H_2PO_4^- in $(\text{H}_2\text{PO}_4)\text{Cr}-\text{R}^+$ can be calculated from $K_{a2}' = K_{a2}K_{f2}/K_{f1}$ if one assumes that K_{f1} has a minor ion pairing component. This calculation gives $10^4 K_{a2}'$ values of 3.5, 0.9, 8.6 and 1.8 for the benzyl, 2-CN, 3-CN and 4-CN complexes, respectively. The magnitude of these values seems reasonable, given the analogous values of $2.2 \times 10^{-4} \text{ M}^{11}$ for $(\text{NH}_3)_5\text{CoOPO}_3\text{H}_2^{2+}$, and $2.3 \times 10^{-3} \text{ M}^{12}$ for $(\text{H}_2\text{O})_5\text{CrOPO}_2\text{H}_2^{2+}$, and that the (R^-) ligand reduces the overall charge and should reduce K_{a2}' . The implication is that the K_{f1} values have a substantial inner-sphere complexation component.

Heterolysis in Aqueous Methylphosphate/Methylhydrogenphosphate. This system was studied with $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ in order to evaluate the influence of ionizable hydrogens on the phosphate. The system can be described by eq 5.7 with the replacement of H_3PO_4 by MeOPO_3H_2 , H_2PO_4^- by MeOPO_3H^- and HPO_4^{2-} by

MeOPO_3^{2-} . In general, methylphosphate is about 10 times less reactive than phosphate. The pH dependence at constant $[\text{MeOPO}_3]_{\text{tot}}$ is shown in Figure 5.4, where it should be noted that the k_{obsd} scale is 10 times smaller than in Figure 5.1.

Least-squares analysis has been used to fit the k_{obsd} values to eq 5.7. The results indicate that K_{f1} is too small to be evaluated, with an upper limit of $\sim 2 \text{ M}^{-1}$ which causes the standard error of the fit to be 12% larger than the best value. If $K_{\text{f1}} < 1$, then the other parameters are reasonably independent of the value assigned to K_{f1} , and one obtains $K_{\text{f2}} = (5.5 \pm 0.5) \times 10^2 \text{ M}^{-1}$, $k_1 = 2.7 \pm 0.17 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = (1.0 \pm 0.09) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and $k_6 = (2.4 \pm 0.38) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$, where uncertainties are the standard error of the parameter and also reflect the range of values for K_{f1} , between 0.1 and 1. In subsequent analysis, we have assumed a value of $K_{\text{f1}} = 0.2 \text{ M}^{-1}$ because it gives a value of K_{a2}' ($7.2 \times 10^{-4} \text{ M}$) for coordinated MeOPO_3H^- in the same range as noted earlier for H_2PO_4^- . The k_6 term was not detected with phosphate, possibly because it is swamped by the much larger k_1 and k_2 with phosphate.

Discussion

In an earlier study^{8b} of the complexation of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{CN}^{2+}$ by various carboxylates, a correlation was noted between the formation constant and the $\text{p}K_{\text{a}}$ of the carboxylic acid. A similar correlation is found here for K_{f1} and K_{f2} for the benzyl complex with the phosphates and acetate as given by eq 5.9, where $\text{p}K_{\text{a}}$ is for the conjugate acid of the complexing anion.

$$\log(K_{\text{f}}) = 0.77 (\text{p}K_{\text{a}}) - 1.82 \quad (5.9)$$

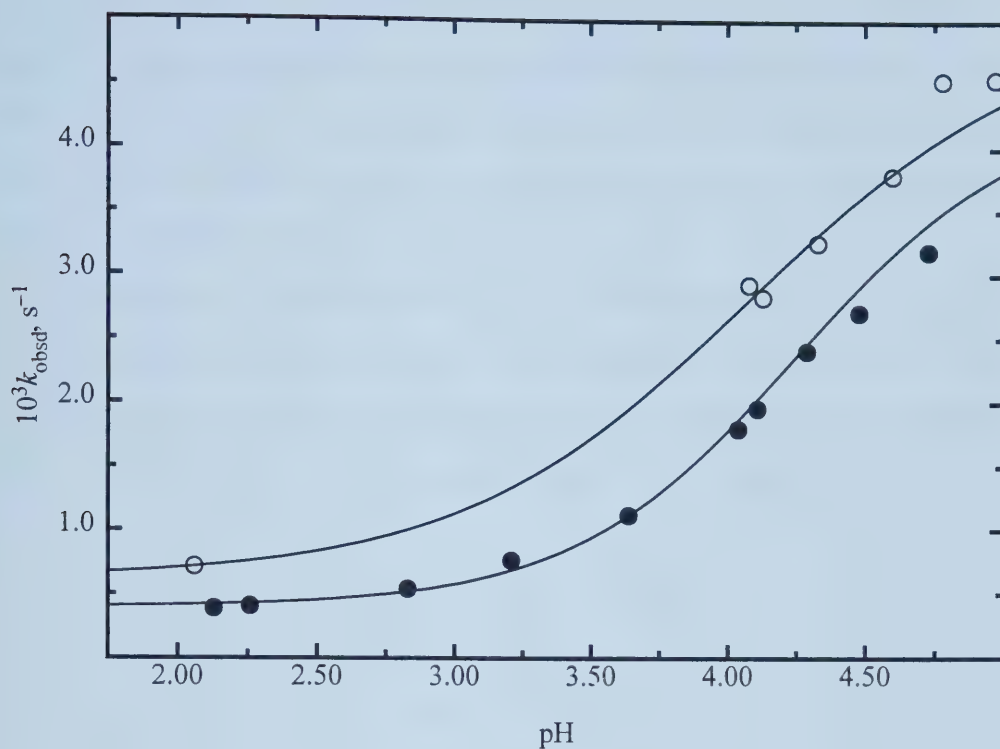
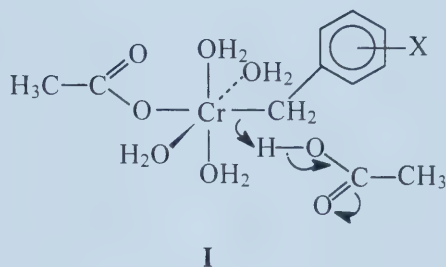


Figure 5.4. Variation of the rate constant for heterolysis of $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$ with pH in methyl phosphate buffers with total phosphate concentrations of 0.30 M (●) and 0.50 M (○) at 25 °C in 1.00 M $\text{NaMeHPO}_4/\text{NaClO}_4$.

The kinetic results yield values for k_1 and k_2 , and the problem is to determine if these can be assigned to a dominant pathway among the kinetically equivalent terms. This will be attempted by assuming that there are rational reactivity relationships between the rate constants for particular pathways which will depend on the properties of the $H_{n-x}A^{x-}$ species involved.

It is simplest to start with the k_7 ($=k_{c1}K_{f1}$) values for the acetate system because there is no reasonable kinetic ambiguity for this pathway. This reaction (k_{c1} term) involves electrophilic attack of acetic acid on the acetato complex and is expected to have a transition state with the general structure of **I**, where X is H, 2-CN,



3-CN or 4-CN. The specific rate constants k_{c1} ($=k_7/K_{f1}$) are given in Table 5.2 and show a relative reactivity of 1: 0.34: 0.19: 0.036 for X = H, 3-CN, 4-CN and 2-CN, respectively. This pattern can be rationalized on the basis of the inductive withdrawing power of the -CN substituent which will make electrophilic attack at CH_2 less favorable. The effect is accentuated by resonance for the 4-CN and 2-CN systems, and the reactivity of the latter may be further reduced by steric inhibition for approach of HOAc to the CH_2 .

The values of k_{c1} provide some upper limits on the other rate constants k_{b1} and k_{b1}' which also involve electrophilic attack by H_3O^+ and HOAc respectively. Since

Table 5.2. Rate Constants for Various Pathway Assignments of the Experimental Rate Constants for Heterolysis of $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{X})^{2+} + \text{H}_n\text{A}$.

H_nA	X	$k_1 \text{ M}^{-1} \text{ s}^{-1}$		$k_2 \text{ M}^{-1} \text{ s}^{-1}$		$k_7 \text{ M}^{-1} \text{ s}^{-1}$
		$10^3 k_{a1}'$	$10^4 k_{a1}$	k_{a2}'	k_{a2}	$10^3 k_{c1}$
HOAc	H	4.4	0.67			19
H_2MePO_4	H	1	0.5	2.7	0.0049	
H_3PO_4	H	44	590	565	0.134	
H_3PO_4	2-CN	9.0	93	65.7	0.046	
H_3PO_4	3-CN	24	650	417	0.082	
H_3PO_4	4-CN	19.3	170	265	0.068	
HOAc	2-CN	12.2	0.95			0.69
HOAc	3-CN	4.15	0.39			6.4
HOAc	4-CN	7.16	0.57			3.7

$k_3 (=k_{b1}K_{f1}K_{a1} + k_{b1}')$ in eq 5.5 is not detected for the acetate-acetic acid system, the implication is that the term of $k_3[\text{H}^+]$ is smaller than that of $k_7K_{a1}[\text{H}^+][\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$, so that

$$k_3 < k_7K_{a1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$$

Since $k_3 = k_{b1}K_{f1}K_{a1} + k_{b1}'$, therefore, the inequality is

$$k_{b1}K_{f1}K_{a1} < k_7K_{a1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$$

$$k_{b1}' < k_7K_{a1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$$

Substitution for $k_7 = k_{c1}K_{f1}$ and rearrangement gives

$$k_{b1} < k_{c1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$$

$$k_{b1}' < k_{c1}K_{f1}K_{a1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$$

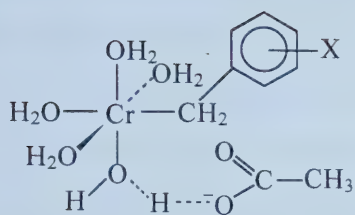
To establish upper limits, one can use the lowest experimental $[\text{OAc}]_{\text{tot}}$ (0.10 M) and pH (~2.0) to calculate that $k_{b1} < 10 k_{c1}$ and $80k_{b1}' < k_{c1}$. The latter inequality indicates that replacement of coordinated acetate in **I** by H_2O reduces the electrophilic reactivity of HOAc by at least 80 times. A parallel argument may be applied to the reactivity of H_3O^+ in the k_{H} and k_{b1} terms to imply the $k_{b1} > 80 k_{\text{H}}$ ($= 80 \times 1.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{CH}_2\text{C}_6\text{H}_5$) which is easily consistent with the upper limit of $10k_{c1}$ ($= 0.19$ for $\text{CH}_2\text{C}_6\text{H}_5$). In other words, the failure to observe a k_3 term in the rate law does not present any anomalies in the reactivity patterns.

The k_7 term could not be evaluated in the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ system, even though H_3PO_4 is ~ 300 times stronger an acid than HOAc. Least-squares analysis including the k_7 term in eq 5.7 provides an upper limit of $< 5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for k_{c1} . This is of the same

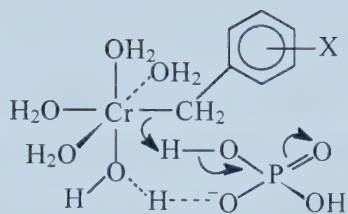
magnitude as k_{c1} with HOAc but does not reflect the greater electrophilicity which might be expected for the more acidic H_3PO_4 . There is a compensating factor in that the K_{f1} for $H_2PO_4^-$ is $\sim 10^2$ smaller than for OAc^- , so that $H_2PO_4^-$ coordination may not enhance the electrophilic susceptibility of the CH_2 as much as OAc^- .

If a common mechanistic pathway is assumed for all of the phosphate systems, then one possibility is to assign $k_2 (= k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2})$ to k_{a1}' and $k_1 (= k_{a2}K_{f2} + k_{a2}')$ to k_{a2}' , so that reaction always involves $(H_2O)_5Cr-R^{2+}$ with some phosphate species. For the benzyl complex, this gives k_{a1}' values of 4.4×10^{-2} , 0.10×10^{-2} and $0.44 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for $H_2PO_4^-$, $MeOPO_3H^-$ and OAc^- , respectively, and k_{a2}' values of 5.65×10^2 and $2.7 \text{ M}^{-1} \text{ s}^{-1}$ for HPO_4^{2-} and $MeOPO_3^{2-}$, respectively. The results for various pathway assignments are shown in Table 5.2. These make no sense in terms of an electrophilic mechanism (analogous to k_{c1}) because the more acidic species, $H_2PO_4^-$ and $MeOPO_3H^-$, are the least reactive, and $MeOPO_3^{2-}$ and OAc^- do not have an electrophilic proton. Furthermore, the rate constants are all larger than the upper limit estimate for the much more acidic H_3PO_4 . With this assignment, the reactivity pattern indicates some type of nucleophilic attack because the more basic species are more reactive. A conjugate base type of mechanism proceeding through a structure such as **II** could be invoked, but then one would expect the more basic acetate ion to be more reactive than $H_2PO_4^-$ which is contrary to the observations. This problem, and the 200 fold reactivity difference between HPO_4^{2-} and $MeOPO_3^{2-}$ lead one to suspect that an ionizable proton is important for transition state reactivity, and the reactive species could be a structure like **III**.

Another possibility is to assign k_1 and k_2 to k_{a2} and k_{a1} , respectively, and the reaction involves $(Y)(H_2O)_4Cr-R + H_2O$, where Y is acetate ion or a phosphate species. The effect of Y would be to increase the electron density at Cr(III) and favor breaking of the Cr-C bond. The values of k_{a2} and k_{a1} are given in Table 5.2.

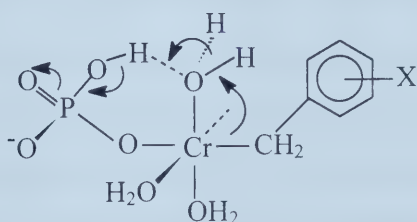


II



III

For the mono and dihydrogen phosphate species, the reactivity parallels the K_f values as might be expected, because stronger complexing should mean more electron donation from Y to Cr(III). But acetate ion and MeOPO_3^{2-} are then much less reactive than expected from their basicity and K_f values. This again points to the importance of an ionizable proton on Y. It is difficult to rationalize how an ionizable proton on the *trans* ligand should greatly affect the reactivity. It conceivably could act through a structure such as **IV**, but the relative basicities of oxygen in coordinated water and phosphate would lead one to expect hydrogen bonding in the opposite sense (ie. $\text{OH}_2 \cdots \text{O-P}$) and **IV** seems a rather unlikely candidate for a highly reactive structure.



IV

Finally, we consider the possibility that k_2 is assigned to k_{b2} . This assignment involves reaction of H_3O^+ with $(\text{HPO}_4)\text{Cr-R}$ or $(\text{MeOPO}_3)\text{Cr-R}$, with k_{b2} values of 168 and $3.8 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for the benzyl complex. Again one is faced with the

difficulty of rationalizing the large kinetic difference due to the replacement of H- by Me- on the *trans* ligand.

The above discussion leaves the impression that there is no coherent assignment for k_1 and k_2 . However, some mild speculation and observations from systems discussed previously do allow some order to be seen in the results. It has been noted above that systems with ionizable protons seem to be unusually reactive, so that one might first concentrate on those ligands without ionizable protons, namely OAc^- , MeOPO_3^{2-} and SO_4^{2-} . It was argued in Chapter 4 that OAc^- was proceeding by the k_{a1}' pathway, based on relative rates for systems with different $-\text{R}$ groups (see Table 4.3). It was not possible to say much about SO_4^{2-} because the lack of a K_f value prevented calculation of k_{a1} from $k_{a1}K_f$ (k_{a1} means k_4 in Chapter 2). However, the $\log(K_f) - \text{p}K_a$ correlation (eq 5.9) allows one to estimate that $K_f \approx 0.10 \text{ M}$, so that $k_{a1} \approx 5.6 \times 10^{-4}$. This makes k_{a1} for SO_4^{2-} 8 times larger than that for OAc^- , contrary to the expectation that the more basic ligand should have the larger k_{a1} , but the k_{a1}' values have the expected relationship with SO_4^{2-} being ~ 80 times smaller than OAc^- . This is consistent with the original assignment for OAc^- , and infers a k_{a1}' assignment also for SO_4^{2-} . Then one might assume the same assignment for MeOPO_3^{2-} , and expect to find a correlation of $\log(k_{ax}') - \text{p}K_a$ for these systems. Such a correlation is found in the form $\log(k_{ax}') = -7.57 + 0.85 \text{ p}K_a - 0.6 Z_{\text{Cr}}Z_{\text{L}}$, where $Z_{\text{Cr}} = +2$ and $Z_{\text{L}} = -1$ for OAc^- , and -2 for MeOPO_3^{2-} and SO_4^{2-} . The last term is added to take into account that charge effects will influence the precursor complex formation in structure **II**. It is noteworthy, but possibly fortuitous, that the coefficient of 0.6 for this term is the value predicted from the standard electrostatic ion pair model, if the ions have an interaction distance of $\sim 3\text{\AA}$. This correlation provides some confirmation for the k_{ax}' assignment for these three anions.

The above correlation equation also allows one to estimate the extra reactivity of the ligands with ionizable protons. For HMeOPO_3^- , H_2PO_4^- and HPO_4^{2-} , the experimental k_{ax}' values are larger than predicted by factors of 1.2×10^2 , 1.6×10^3 and 62, respectively. The bifunctional mode of operation proposed for these species (structure **III**) predicts that the effectiveness might go through a maximum as the $\text{p}K_{\text{a}}$ increases. Greater basicity favours interaction with the *cis*- H_2O ligand, but makes the proton on the anion a poorer electrophile for the organo-ligand. These observations provide a hint that the optimum rate enhancement might be found for an anion with a ionizable proton with a $\text{p}K_{\text{a}}$ in the 2 - 4 range.

Much of this discussion has emphasized the involvement of *cis*- H_2O ligands, but it should be acknowledged that there is conflicting evidence on this involvement from other systems. Earlier, Ogino et al.¹³ and Rotman et al.^{4b} found that the EDTA complexes of Cr-R undergo heterolysis at rates similar to the parent pentaqua complex, and suggested that *cis*- H_2O ligands are not important. Recently, Espenson and co-workers^{14,15} found that the *trans*- $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})\text{Cr}-\text{R}^{2-}$ complexes are very resistant to heterolytic cleavage by H_2O or H_3O^+ and suggested that *cis*- H_2O ligands are important for heterolytic reactivity. More relevant to the present work are the reports of Cohen and co-workers^{4b,c} that the heterolysis of *trans*- $([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})\text{Cr}-\text{R}^{2+}$ ($\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$ or CH_2OH) is catalysed by acetate ion, but there are several problems with these reports. Our analysis indicates that the published data^{4b} ($\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$) do not adequately fit the expected rate law. Least-squares analysis gives a best-fit in which 7 of the 18 experimental rate constants deviate by more than 20 % from the predicted best-fit value. The protolytic equilibrium at pH 4–6 found by Espenson et al.¹⁴ for analogous systems was not reported by Cohen et al. for either system in acetate buffers. The spectrum published by Cohen et al.^{4b} of the complex with $\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$ is quite different from that reported by Espenson et al.¹⁵ for $\text{R} = \text{CH}_2\text{OH}$ and

CHCH₃OH. Espenson et al.¹⁵ were unable to isolate the complex with R = C(CH₃)₂OH, and attributed this to rapid homolysis.¹⁶ They found that the R = CHCH₃OH complex undergoes decomposition by β -elimination, and the same may be true for R = C(CH₃)₂OH. The data^{4b} and graphs^{4c} presented by Cohen et al. indicate that decomposition in the absence of acetate ion has k_{obsd} of ~ 0.04 and $\sim 0.2 \text{ s}^{-1}$ at pH 5.1 for R = CH₂OH and C(CH₃)₂OH, respectively. However, Espenson et al.¹⁵ found negligible decomposition in 6 h in acidic solution for R = CH₂OH. This shows that the decomposition at pH 5.1 cannot be due to heterolysis of *trans*-([15]aneN₄)(H₂O)Cr-CH₂OH²⁺, and is probably a reaction of *trans*-([15]aneN₄)(OH)Cr-CH₂OH⁺.

The overall picture that emerges from our results is that the dominant factor influencing the reactivity enhancement for heterolysis is the basicity of the H_{*n-x*}A^{x-} species. However, a comparison of the H_{*n-x*}A^{x-} with ionizable protons and the fully deprotonated species Aⁿ⁻ reveals that the former are substantially more reactive than expected from basicity considerations. This is most consistent with a reactive state like **III** for the H_{*n-x*}A^{x-} species with k_2 and k_1 assigned to k_{a1}' and k_{a2}' . It should be noted that the 2-CN complex has the smallest rate constant with this choice and the reactivity pattern parallels that of k_{c1} for HOAc. This might be expected on the basis of the structural similarity of **I** and **III**.

Experimental Section

Materials. Aqueous solutions of [(H₂O)₅Cr-CH₂C₆H₄X]²⁺ (X = H, 2-CN, 3-CN and 4-CN) were prepared by mixing 40 mL of deoxygenated methanol containing 2 mmol of the appropriate benzyl bromide (Aldrich) with 20 mL of aqueous 0.3 M chromium(II) perchlorate, prepared by amalgamated zinc reduction of aqueous chromium(III) perchlorate. After ~ 10 min at ambient temperature the solution had

changed from pale blue to dark greenish yellow, and it was loaded onto a column (8×2 cm) of Dowex 50W-X2(200) ion exchange resin in either the H^+ or Na^+ form under an argon atmosphere at 0°C . Excess Cr(II) was eluted with 0.6 M NaClO_4 in 0.01 M HClO_4 , and the desired product was eluted with 1.0 M NaClO_4 in 0.01 M HClO_4 . The product was stored at -10 to -15°C . Tests with the 4-CN system showed that the mixture before ion exchange gives the same decomposition kinetics as the purified solution.

The acetate/acetic acid buffers were prepared from solutions of sodium acetate trihydrate (BDH) by adding standardized perchloric acid to obtain the desired pH. The initial solutions contained enough sodium perchlorate to give a final ionic strength of 1.0 M . The phosphate buffers were prepared similarly from NaH_2PO_4 (Fisher) by adding sodium hydroxide or HClO_4 to obtain the desired pH. The disodium methylphosphate was prepared by reaction of aqueous Na_3PO_4 with dimethylsulfate as described by Bailly.¹⁷ The barium salt was isolated by addition of BaCl_2 and converted to the sodium salt by treatment with Na_2SO_4 . The concentration of $\text{Na}_2\text{MeOPO}_3$ in stock solutions was determined by titration with standardized HCl using methyl orange indicator. Sodium perchlorate and HClO_4 were added to these solutions to obtain the desired ionic strength and pH (± 0.002).

Kinetic Measurements. The absorbance decrease at 356 nm was followed on a Hewlett Packard 8451 diode array spectrophotometer equipped with a thermostated cylindrical cell holder and standard water circulating temperature control system. A 50 mm cylindrical quartz cell was used throughout. For the heterolysis reaction, 10 mL of buffer and sodium perchlorate, to control ionic strength, were placed in the cell, sealed with serum caps and deoxygenated for 20 min by bubbling purified argon. Then syringes were used to add aqueous chromium(II) perchlorate and $[(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2+}$ to give final concentrations of $2 \times 10^{-3}\text{ M}$ and $(0.6-1) \times 10^{-4}\text{ M}$,

respectively. The absorbance-time data typically involved 80 points over 5–6 half-lives, and were analysed by nonlinear least-squares to a first-order model.

The dependence of the experimental rate constants on pH and H_nA concentration has been analysed by standard least-squares methods and the errors quoted are one standard deviation. For this analysis the following pK_a^{18} values were used: HOAc, 4.73; H_3PO_4 , 2.12, $H_2PO_4^-$, 7.21; $MeOPO_3H_2$, 1.54, $MeOPO_3H$, 6.31.

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Chapter 6. Kinetics of Dissociation of Iron(III) Complexes of Tiron in Aqueous Acid*

Introduction

There have been numerous studies¹ on the complexation of aqueous iron(III), and the general conclusion is that $\text{Fe}(\text{OH}_2)_6^{3+}$ is much less reactive than its conjugate base, $(\text{H}_2\text{O})_5\text{Fe}(\text{OH})^{2+}$, and that the latter reacts by dissociative activation, while the former shows associative characteristics. There are far fewer studies on the substitution reactivity of other iron(III) complexes and therefore the reactivity and mechanistic effects of other ligands on the iron(III) center are not well characterized. The main exception to this generalization are the hydroxamic acid complexes that are models for desferrioxamine B. These have been the subject of several studies by Crumblis and co-workers^{2,3} and Birus and co-workers.^{4,5} The hydrolysis of the tris, bis and mono acetohydroxamate complexes has been kinetically characterized by Birus et al.⁵ and the pressure dependence has been reported recently.⁴

Iron(III) catechol complexes have been widely investigated by Raymond and co-workers⁶ as models for the siderophile enterobactin, and by Que and co-workers⁷ as dioxygenase models. The simple catechol systems are less amenable to systematic hydrolysis studies because of redox instability involving iron(III) or iron(III) and dioxygen. However, the early work of McBryde⁸ indicates that this should not be a problem with Tiron (1,2-dihydroxy-3,5-benzenesulfonate). The mono, bis and tris complexes are readily distinguished spectrophotometrically, and the formation constants

* A version of this chapter has been accepted. Zhang, Z.; Jordan, R. B. *Inorg. Chem.* 1995.

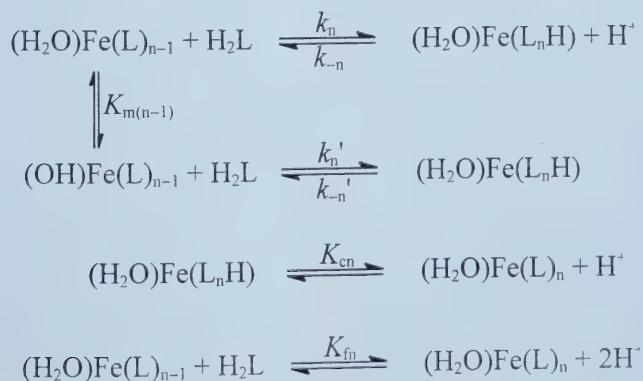
should allow for their independent study by an appropriate choice of starting pH and Tiron concentration. The present study was undertaken to determine the reactivity patterns of these catecholate complexes.

Since monodentate protonated catecholate complexes of iron(III) have been proposed as critical intermediates in dioxygenase models,^{7,9} it was also of interest to determine if such species might be characterized by the kinetic analysis. Que and co-workers¹⁰ first structurally characterized such a complex, and another example has been reported recently by Kitajima et al.¹¹

Results

Preliminary experiments confirmed McBryde's earlier observations that the tris-, bis- and mono-Tiron complexes of iron(III) are readily distinguished spectrophotometrically. This is shown, along with the time evolution, in Figures 6.1–6.2. The wavelengths of the absorbance maxima increase progressively from the tris to bis to mono complexes, and the excellent isosbestic behavior for the tris-bis and bis-mono conversions also is shown in Figures 6.1–6.2. After analysing the kinetic results for all three reactions, it appears that they can be described in general by Scheme I,

Scheme I



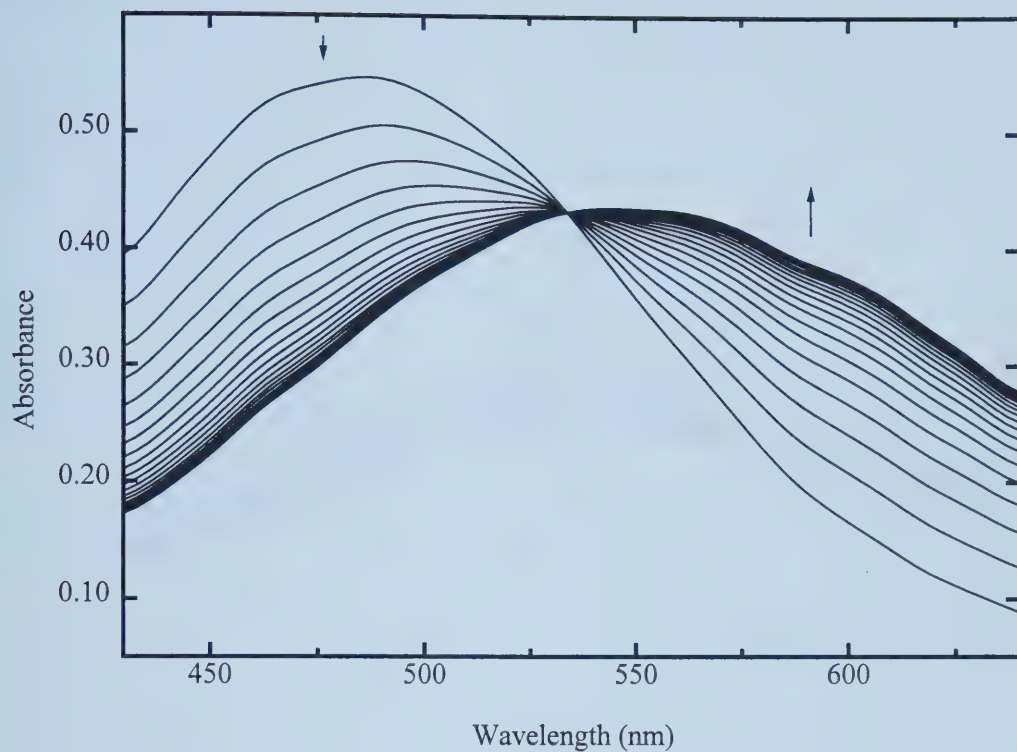


Figure 6.1. Variation of absorbance with time and wavelength for the conversion of tris to bis-Tiron complexes of aqueous iron(III) at pH 4.8 in 0.02 M acetate buffer and 1.0 M $\text{HClO}_4/\text{NaClO}_4$ at 14.0 °C with 0.01 s time intervals: the final total concentrations are for iron(III) = 9.6×10^{-5} M and Tiron = 5.8×10^{-4} M.

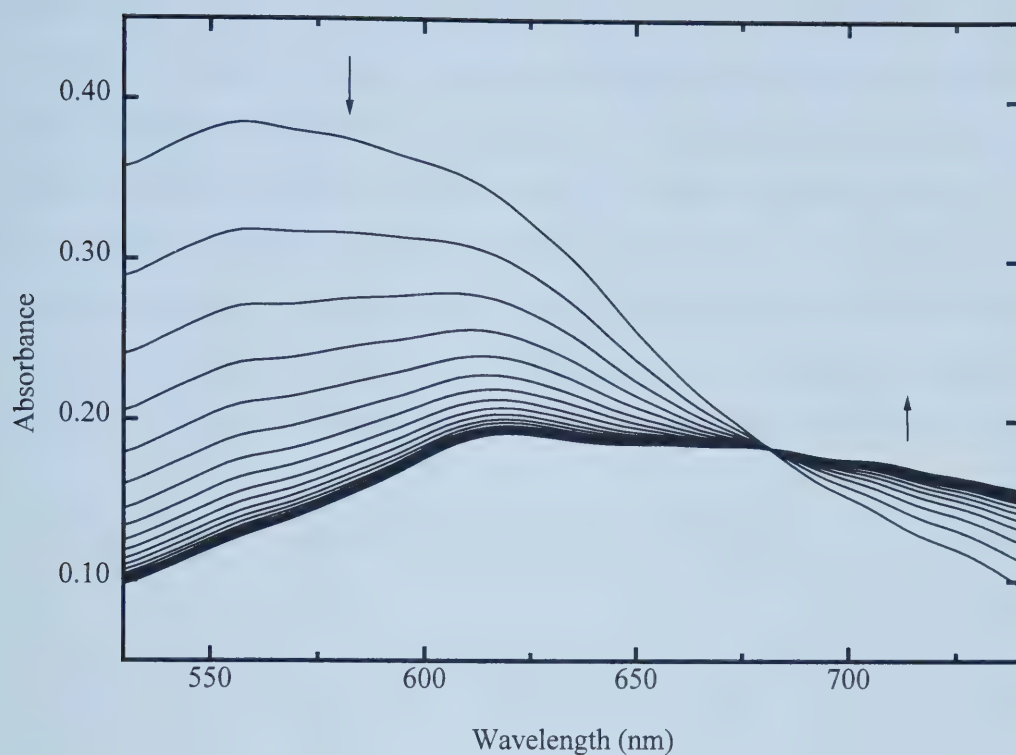


Figure 6.2. Variation of absorbance with time and wavelength for the conversion of bis to mono-Tiron complexes of aqueous iron(III) in 1.0 M $\text{HClO}_4/\text{NaClO}_4$ at 14.0 °C with 0.01 s time intervals: the final total concentrations are for $[\text{H}^+] = 1.53 \times 10^{-3}$ M, iron(III) = 9.6×10^{-5} M and Tiron = 5.8×10^{-4} M.

where H_2L represents the Tiron dianion protonated on the OH groups, only one of the possible water ligands is included, and charges are omitted for generality. It should be noted that the reaction described by K_{cn} might be proton dissociation from a protonated chelate, or chelation of the monodentate form of the catechol derivative with proton loss. Therefore it may involve both deprotonation and chelation. The predicted first-order rate constant for Scheme I is given by eq 6.1 or 6.2 (the derivation of eq 6.1 and 6.2 is given in Appendix 6.4), in terms of either the complex formation rate constants (k_n) or the dissociation constants (k_{-n}), where $[H_2L]$ represents total uncomplexed Tiron

$$k_{\text{obsd}} = (k_n[H^+] + k_n'K_{m(n-1)}) \left\{ \frac{[H_2L]}{K_{m(n-1)} + [H^+]} + \frac{K_{cn}[H^+]}{K_{fn}(K_{cn} + [H^+])} \right\} \quad (6.1)$$

$$k_{\text{obsd}} = (k_{-n}[H^+] + k_{-n}') \left\{ \frac{K_{fn}[H_2L]}{K_{cn}(K_{m(n-1)} + [H^+])} + \frac{[H^+]}{(K_{cn} + [H^+])} \right\} \quad (6.2)$$

which is in the protonated form at the acidities of most of this study. The forward and reverse rate constants are related to the equilibrium constants by eq 6.3. The predicted k_{obsd} has various limiting forms depending on the magnitudes of K_{cn} and $K_{m(n-1)}$ relative

$$\frac{k_n}{k_{-n}} = \frac{K_{fn}}{K_{cn}} = \frac{k_n'}{k_{-n}'} K_{m(n-1)} \quad (6.3)$$

to $[H^+]$ and the magnitudes of K_{cn} and K_{fn} . The forms required to fit the dissociation kinetics of the mono, bis and tris complexes will be discussed individually.

Dissociation Kinetics of $(H_2O)Fe(L)$. This reaction was followed at 670 nm, in the region of the broad absorbance maximum for the complex, by mixing a solution of Tiron $((1.6-1.8) \times 10^{-3} \text{ M})$ and $Fe(ClO_4)_3$ $(2 \times 10^{-4} \text{ M})$ at pH 2.7-3 with an equal volume of a solution of $HClO_4/NaClO_4$ at concentrations to give the required final

acidity and 1.00 M ionic strength. The $[H^+]$ range was 0.05 to 0.5 M at temperatures of 2.0, 14.0, 25.0 and 36.7 °C, and the experimental first-order rate constants, k_{obsd} , are given in Appendix 6.1.

The variation of k_{obsd} with $[H^+]$ in terms of Scheme I at the four temperatures proved to be more complex than would appear from any one temperature. The problem is illustrated by the plots in Figure 6.3. At 36.7 °C, the k_{obsd} versus $[H^+]$ plot shows a slight leveling at higher $[H^+]$, at 25 °C the plot is essentially linear but shows increasing upward curvature at 14.0 and 2.0 °C, respectively. In eq 6.1 or 6.2, the second term in curled brackets dominates, and the leveling at higher $[H^+]$ and 36.7 °C would indicate that $[H^+] \geq K_{c1}$ and that $k_{-1}' > k_{-1}[H^+]$. However, the upward curvature at the lower temperatures implies that $[H^+] \leq K_{c1}$ and that $k_{-1}[H^+]$ is contributing significantly. With the assumption that a uniform rate law applies at all temperatures, this behavior can only be accounted for by the temperature variation of the various parameters being such that different approximate limiting conditions apply at the temperature extremes. Therefore, the k_{obsd} values at all temperatures were fitted by assuming that the temperature dependence of the rate constants is described by the transition state equation, and the equilibrium constants by the usual thermodynamic relationship. The temperature dependence of K_{m0} is known independently and was taken from values given by Baes and Messmer.¹² The resulting fit is very good, and the experimental and calculated values of k_{obsd} are given in Appendix 6.1.

The best fit values of ΔH^* and ΔS^* and of the standard ΔH° and ΔS° are given in Table 6.1. At 25 °C, the predicted values are: $k_{-1} = 1.18 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1}' = 1.28 \text{ s}^{-1}$, $K_{\text{f1}} = 2.0 \text{ M}$ and $K_{c1} = 0.96 \text{ M}$. These values can be combined in eq 6.3 to calculate the formation rate constants at 25 °C as: $k_1 = 2.3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_1' = 1.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (using $K_{m0} = 1.6 \times 10^{-3} \text{ M}$). Similar combination can be used to obtain the ΔH^* and ΔS^* for k_1

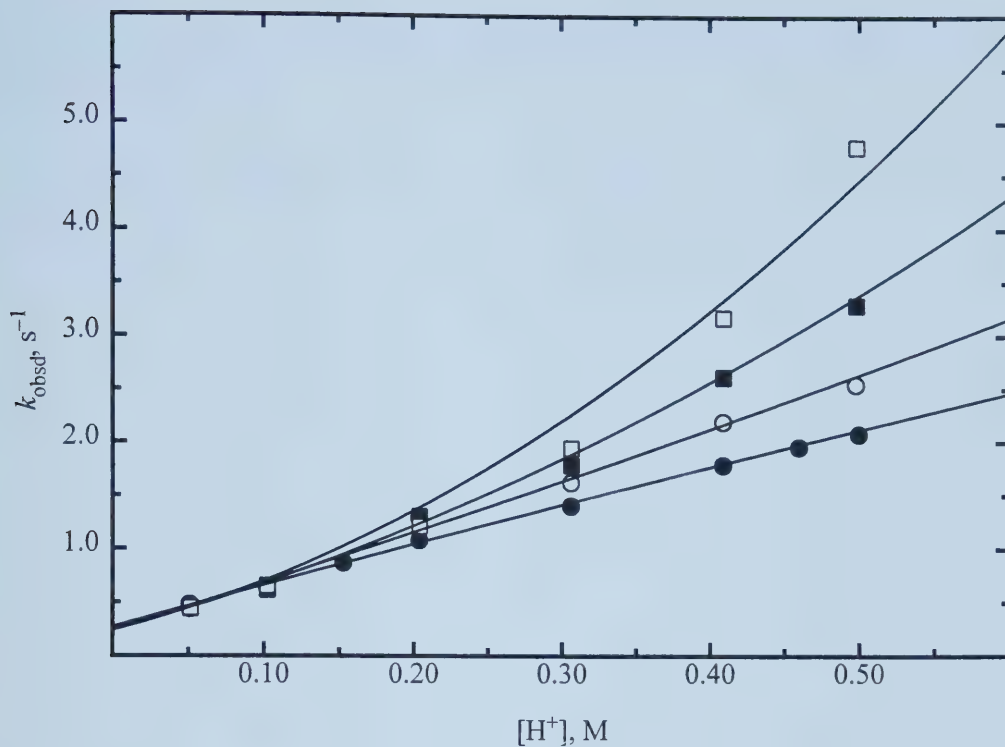


Figure 6.3. Variation of the first order rate constant for dissociation of the mono-Tiron complex of iron(III) with $[\text{H}^+]$ at 2.0 (□), 14.0 (■), 25.0 (○) and 36.7 °C (●). Values have been scaled to the same magnitude by multiplying by factors of 85, 17 and 4.2 at 2.0, 14.0 and 25.0 °C, respectively.

Table 6.1. Summary of Results for the Reactions of the Iron(III)–Tiron System in 1.0 M HClO₄/NaClO₄

Parameter	Value (25 °C)	ΔH° , kcal mol ⁻¹	ΔS° , cal mol ⁻¹ K ⁻¹
k_1^b	2.3	8.89	-27.05 ^e
k_{-1}	1.18	4.04 ± 1	-44.8 ± 3
$k_1'^b$	1.7 × 10 ³	10.1	-9.9
k_{-1}'	1.28	14.2 ± 0.2	-10.4 ± 1
K_{c1}	0.96	-9.99 ± 1	-33.6 ± 3
K_{f1}	2.01	-5.14 ± 1	-15.85 ^e ± 3.4
k_2^b	3.2 × 10 ³	19.2	21.9
k_{-2}/K_{c2}	1.88 × 10 ⁷	19.89 ± 0.03	41.46 ^e ± 1.6
k_{-2}^c	>2.8 × 10 ⁵		
k_{-2}'/K_{c2}	1.85 × 10 ³	1.41 ± 6	-38.84 ^e ± 18
$k_{-2}'^c$	>2.8 × 10 ¹		
K_{c2}	>0.015		
K_{f2}^d	1.7 × 10 ⁻⁴	(-0.7)	(-19.59)
k_3	7.7 × 10 ³	15.83 ± 0.06	12.3 ± 3.2
k_{-3}	1.7 × 10 ⁷	16.2 ± 0.16	28.9 ± 0.075
K_{c3}	7.4 × 10 ⁻⁵	4.1 ± 1	-5.1 ± 4
K_{f3}	3.35 × 10 ⁻⁸	3.7	-21.7

^a These are activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for rate constants and ΔH° and ΔS° for equilibrium constants. ^bCalculated from $k_n = k_{-n}K_{fn}/K_{cn}$ and $k_n' = k_{-n}'K_{fn}'/(K_{cn}K_{m(n-1)})$. ^c Lower limits estimated from the lower limit on K_{c2} . ^d ΔH° estimated from values for K_{f1} and K_{f3} and using the K_{f2} reported by McBryde at 25 °C to obtain ΔS° . ^e The extra significant figure avoids round-off error by recalculation.

and k_1' given in Table 6.1. The value of K_{f1} is in good agreement with that of 1.8 M determined by McBryde,⁸ and k_1' agrees with the values of 2.1×10^3 and $2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ determined from formation kinetics by Mentasti et al.¹³ and Chatlas and Jordan,¹⁴ respectively.

Dissociation Kinetics of $(\text{H}_2\text{O})\text{Fe}(\text{L})_2$. This reaction was studied at 562 nm by mixing solutions of $\text{Fe}(\text{ClO}_4)_3$ ($1.0 \times 10^{-4} \text{ M}$) and Tiron ($2.6 \times 10^{-4} \text{ M}$) at pH 4.3 with an equal volume of appropriate solutions of $\text{HClO}_4/\text{NaClO}_4$. Measurable rates were obtained for $[\text{H}^+]$ between 1.5×10^{-3} and $1.4 \times 10^{-2} \text{ M}$ at 2.0, 9.0 and 14.0 °C. The acidities are lower for the bis compared to the mono complex because of the faster hydrolysis of the bis complex. The experimental k_{obsd} values are given in Appendix 6.2 and plotted in Figure 6.4.

From Figure 6.4, it is apparent that k_{obsd} has essentially a second order dependence on $[\text{H}^+]$ at all three temperatures. However, the k_{obsd} values at low $[\text{H}^+]$ are under-predicted by a simple $[\text{H}^+]^2$ dependence, and this is shown by the $k_{\text{obsd}} [\text{H}^+]^{-2}$ plot in Figure 6.5. This should give a horizontal line for a purely $[\text{H}^+]^2$ dependence, but the plots have a persistent positive slope with a slight temperature dependence. This slope indicates the not unusual feature that there is another term in the rate law which becomes significant at low $[\text{H}^+]$, but the difficult feature turns out to be the small temperature dependence of this term.

There are three models that can explain the $[\text{H}^+]$ dependence of k_{obsd} . In terms of Scheme I, if the second term in curled brackets in eq 6.1 or 6.2 is dominant, and $K_{c2} \gg [\text{H}^+]$ (because the $[\text{H}^+]^2$ dependence shows no attenuation at the highest $[\text{H}^+]$ values), then eq 6.2 reduces to eq 6.4 from which only values of k_{-2}/K_{c2} ($= k_2/K_{f2}$) and k_{-2}'/K_{c2} ($= k_2'K_{m1}/K_{f2}$) can be determined. Least-squares analysis of the k_{obsd} values at all

$$k_{\text{obsd}} = \left(\frac{k_{-2}[\text{H}^+]}{K_{c2}} + \frac{k_{-2}'}{K_{c2}} \right) [\text{H}^+] \quad (6.4)$$

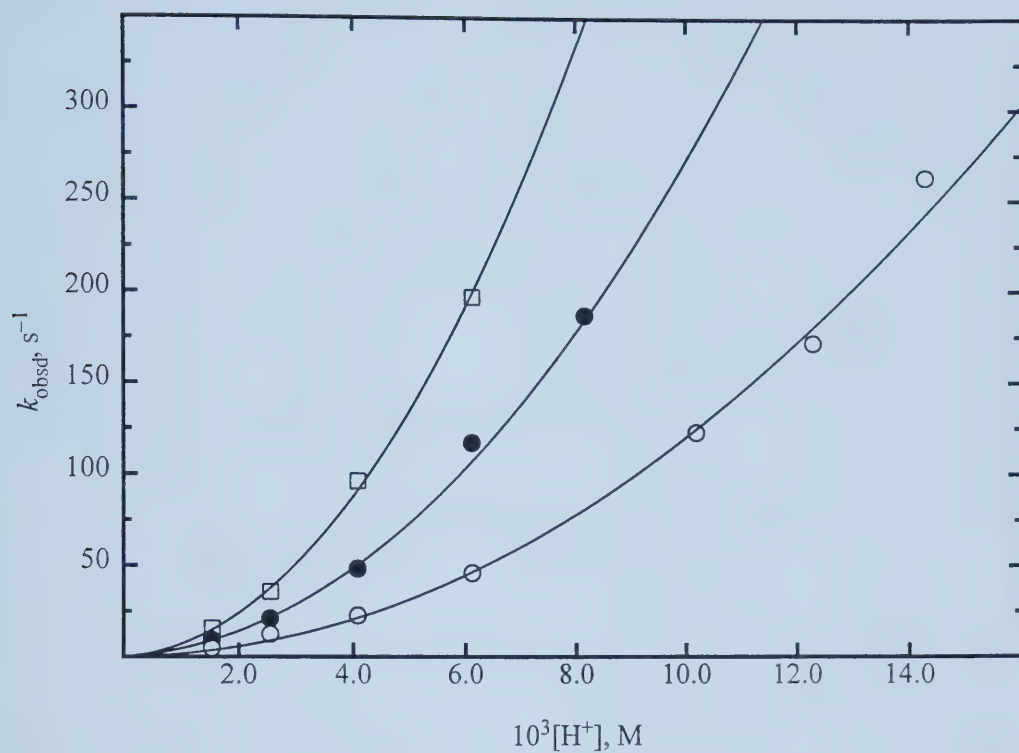


Figure 6.4. Variation of the first order rate constant for dissociation of the bis-Tiron complex of iron(III) with $[\text{H}^+]$ at 2.0 (○), 9.0 (●) and 14.0 °C (□).

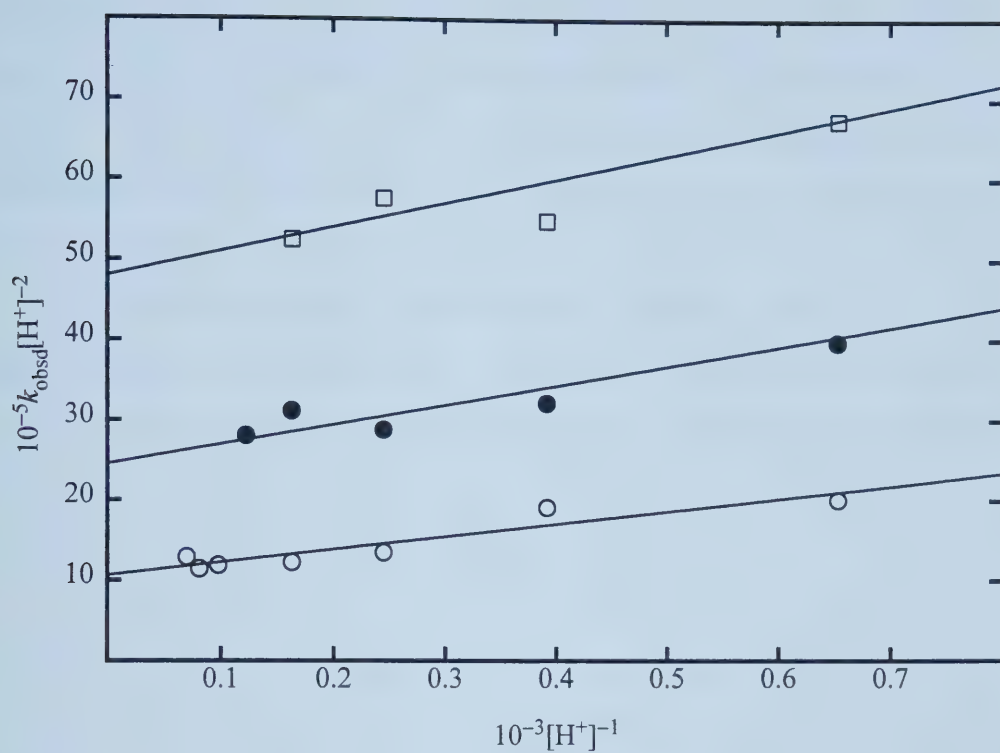


Figure 6.5. Variation of $k_{\text{obsd}}[\text{H}^+]^{-2}$ with $[\text{H}^+]^{-1}$ for dissociation of the bis-Tiron complex of iron(III) at 2.0 (○), 9.0 (●) and 14.0 °C (□).

three temperatures gives apparent activation parameters ΔH^* (kcal mol⁻¹) and ΔS^* (cal mol⁻¹ K⁻¹) of 19.8 ± 0.37 and 41.2 ± 1.8 for k_{-2}/K_{c2} , and 4.2 ± 4.7 and -28.5 ± 16 for k_{-2}'/K_{c2} . The parameters for k_{-2}'/K_{c2} are poorly defined because this term makes a small contribution, as can be seen from Figure 6.4. At 25 °C, the predicted values are $k_{-2}/K_{c2} = 1.9 \times 10^7$ and $k_{-2}'/K_{c2} = 3 \times 10^3$.

There is another form of eq 6.2 which gives an equally good fit of the data. If the k_{-2}' contribution is negligible, $K_{c2} \gg [H^+]$, and $K_{m1} \ll [H^+]$, then eq 6.2 simplifies to eq 6.5. Least-squares analysis as before, gives apparent ΔH^* (kcal mol⁻¹) and ΔS^*

$$k_{\text{obsd}} = \frac{k_{-2}[H^+]}{K_{c2}} \left(\frac{K_{f2}[H_2L]}{[H^+]} + [H^+] \right) \quad (6.5)$$

(cal mol⁻¹ K⁻¹) of 18.87 ± 0.03 and 38.0 ± 1.3 for k_{-2}/K_{c2} , and ΔH° and ΔS° of -15.5 ± 2.6 and -68.6 ± 8 for K_{f2} . The predicted values at 25 °C are: $k_{-2}/K_{c2} = 1.8 \times 10^7$ M⁻² s⁻¹ and $K_{f2} = 2.4 \times 10^{-4}$ M. The value of K_{f2} is in good agreement with that of 1.7×10^{-4} M determined by McBryde.⁸ Despite this agreement, there is an anomaly with this model because the magnitude of ΔH° is so large. Such values are more typically in the ± 5 kcal mol⁻¹ range, as found above for K_{f1} and below for K_{f3} .

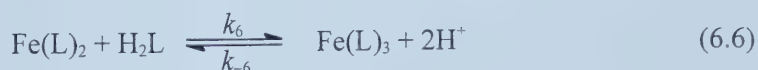
Since the K_{f2} determined from eq 6.5 is of the correct magnitude, it appears that the term containing this factor in eq 6.2 is of some significance. However, it is unrealistic to expect to extract the temperature dependence of k_{-2}/K_{c2} , k_{-2}'/K_{c2} and K_{f2} from the data. Therefore the data have been fitted to the simplified version of eq 6.2 (assuming $K_{c2} \gg [H^+]$, and $K_{m1} \ll [H^+]$) by taking⁸ $K_{f2} = 1.7 \times 10^{-4}$ M at 25 °C with $\Delta H^\circ = -0.7$ kcal mol⁻¹, intermediate between the values for K_{f1} and K_{f3} . Least-squares analysis gives the apparent ΔH^* and ΔS^* for k_{-2}/K_{c2} , and k_{-2}'/K_{c2} summarized in Table 6.1. As expected, the parameters for k_{-2}'/K_{c2} are poorly defined. The experimental and

calculated values of k_{obsd} are given in Appendix 6.2. The predicted values at 25°C are $1.88 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$ and $1.85 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for k_{-2}/K_{c2} and k_{-2}'/K_{c2} , respectively.

Dissociation Kinetics of Fe(L)_3 . This reaction was studied by mixing a solution of $\text{Fe}(\text{ClO}_4)_3$ ($1.92 \times 10^{-4} \text{ M}$) and Tiron ($1.16 \times 10^{-3} \text{ M}$) at pH 6.64 with an equal volume of a solution of 0.04 M acetate buffer adjusted to the desired pH (4.5–5.7), with both solutions in 1.0 M NaClO_4 . The disappearance of the red tris-complex was monitored at 482 nm, but the same rate constant was obtained by observing the appearance of the blue bis-complex at 562 nm. Variation of the total acetate concentration between 0.01 and 0.1 M had no effect on the kinetic observations. The results are given in Appendix 6.3.

It should be noted that the analysis of this reaction has been slightly modified. Firstly, to take into account the first ionization of Tiron ($\text{p}K_{a1} 7.17$), the total Tiron concentration is $[\text{H}_2\text{L}]_t = [\text{H}_2\text{L}] + [\text{HL}]$, and then $[\text{H}_2\text{L}] = [\text{H}^+][\text{H}_2\text{L}]_t (K_{a1} + [\text{H}^+])^{-1}$. Secondly, the analysis with various models indicates that there is no contribution from a hydrolysed species (ie. $K_{m2} \ll [\text{H}^+]$ in Scheme I).

The values of k_{obsd} and their variation with $[\text{H}^+]$ are shown in Figure 6.6. It is clear that the rate has a higher than first-order dependence on $[\text{H}^+]$. In fact, it is close to an $[\text{H}^+]^2$ dependence, and this could be consistent with the simple reaction in eq 6.6.



This predicts that $k_{\text{obsd}} = k_{-6}[\text{H}^+]^2 + k_6[\text{H}^+][\text{H}_2\text{L}]_t(K_{a1} + [\text{H}^+])^{-1}$. However, the fit is at best adequate, since 10 of the 21 predicted values are >10 % different from the experimental values.

The results can be fitted by Scheme I with the modifications noted above for Tiron ionization and omission of coordinated water ionization. The analysis also shows

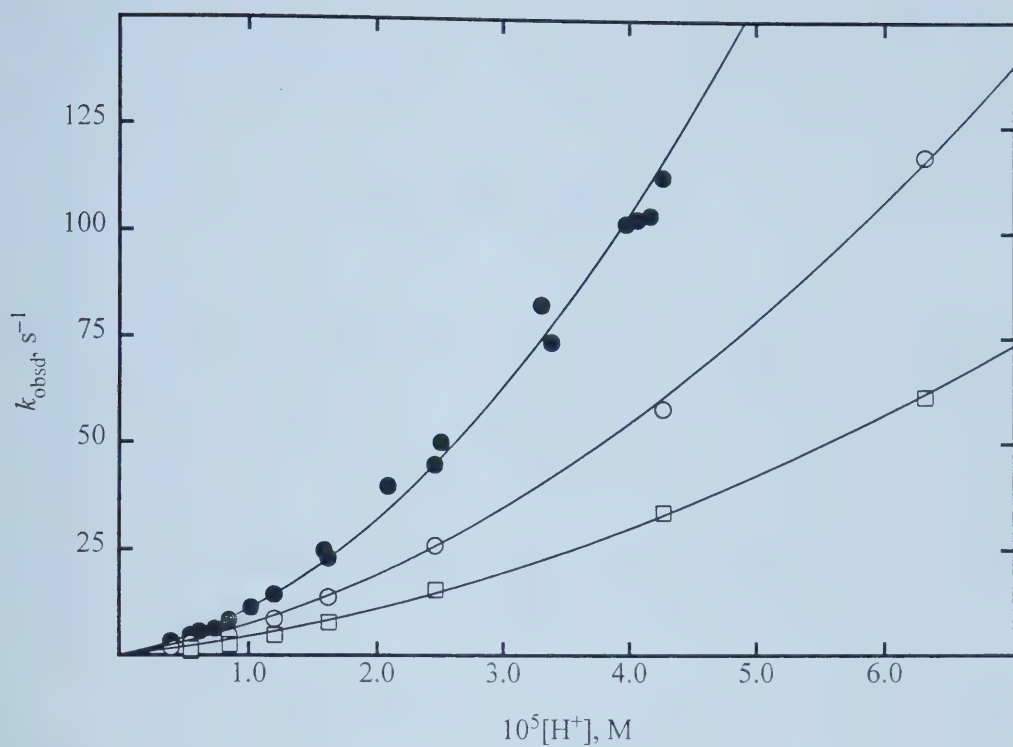


Figure 6.6. Variation of the first order rate constant for dissociation of the tris-Tiron complex of iron(III) with $[\text{H}^+]$ at 1.8 (□), 8.0 (○) and 14.5 °C (●).

that the k_3' path is not required to fit the results. Then eq 6.1 can be simplified and modified by the substitution $k_3 K_{c3}/K_B = k_{-3}$ to obtain eq 6.7. The results were

$$k_{\text{obsd}} = \frac{k_3 [\text{H}^+][\text{H}_2\text{L}]_t}{K_{a1} + [\text{H}^+]} + \frac{k_{-3} [\text{H}^+]^2}{K_{c3} + [\text{H}^+]} \quad (6.7)$$

analysed by least-squares fitting to eq 6.7 with k_3 , k_{-3} , and K_{c3} as parameters at each of the temperatures of 14.5, 8.0 and 1.8 °C and found to give good fits (as shown in Appendix 6.3) with sensible temperature dependencies for each parameter. The fits are much better than those to the model based on eq 6.6, with a 2.3 times smaller standard error of the fit. The best fit ΔH^* and ΔS^* and ΔH° and ΔS° are given in Table 6.1. The predicted values at 25 °C are: $k_3 = 7.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-3} = 1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $K_{c3} = 7.4 \times 10^{-5} \text{ M}$. From these one can calculate that $K_B = 3.35 \times 10^{-8} \text{ M}$ at 25 °C, in reasonable agreement with $2.7 \times 10^{-8} \text{ M}$ determined by McBryde,⁸ and the ΔH values and K_B at 25 °C can be combined to give the ΔH° and ΔS° for K_B in Table 6.1.

Discussion

A major purpose of this study is to provide some indication of general reactivity patterns for mono, bis and tris complexes of catechol ligands with aqueous iron(III). The results are collected in Table 6.1. As already noted, the equilibrium constant values (K_{fn}) from the kinetics are in good agreement with previously determined values.⁸ There also is good agreement on the rate constant for formation of the mono iron(III)-Tiron complex from $\text{Fe}(\text{OH})^{2+} + \text{H}_2\text{L}$. The present work has added the rate constant for $\text{Fe}(\text{OH}_2)^{3+} + \text{H}_2\text{L}$ and the activation parameters for both reactions.

One noteworthy feature is that the k_n' pathway for the hydrolysed species $(\text{HO})\text{Fe}(\text{L})_{n-1}$ is important only for $n = 1$. It is well established that substitution on

aqueous iron(III) is dominated by the reactivity of $(\text{H}_2\text{O})_5\text{Fe}(\text{OH})^{2+}$, but this pathway is barely detectable for $(\text{HO})\text{Fe}(\text{L})$ and of no influence for $(\text{HO})\text{Fe}(\text{L})_2$. This may occur because complexation by the catecholate reduces the charge on the iron(III) and thereby reduces the hydrolysis constant ($K_{\text{m}(n-1)}$) to an extent that the hydrolysed species is no longer present at kinetically significant concentrations. Another factor is that the k_n pathway dominates for $n > 1$ because k_2 and k_3 are $>10^3$ times larger than k_1 . It appears that complexation by one or two catecholate ligands provides enough labilization so that the effect of an OH^- ligand is attenuated.

The large difference between k_1 and k_2 or k_3 appears to reflect a mechanistic change. For k_1 , the $\Delta S^\ddagger$ is very negative, consistent with the commonly assumed associative activation for substitution of $\text{Fe}(\text{OH}_2)_6^{3+}$, but the $\Delta S^\ddagger$ values for k_2 and k_3 are positive and this overcomes the higher $\Delta H^\ddagger$ to make these rate constants much larger than k_1 . It seems reasonable that the catecholate ligand(s) would favor dissociative activation for k_2 and k_3 by lowering the effective charge on the iron(III) and favoring dissociation of a water ligand. This factor also would disfavor associative nucleophilic attack on the complexed iron(III).

The reverse reactions must have the same mechanistic assignment as the forward reaction. The very negative $\Delta S^\ddagger$ value for k_{-1} and positive value for k_{-3} are consistent with associative and dissociative activation, respectively, and this is consistent with the assignments above for k_1 and k_3 . Although k_{-2} is not independently defined, the large positive $\Delta S^\ddagger$ for k_{-2}/K_{c2} suggests that the $\Delta S^\ddagger$ for k_{-2} is positive and that this pathway is dissociatively activated. The dissociation rate constants also show a large ($>10^5$) increase between k_{-1} and k_{-2} , indicative of a mechanistic change.

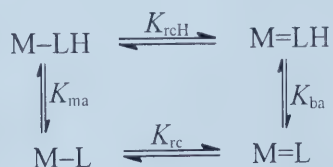
The rate constants for Tiron and two hydroxamic acids reacting with aqueous iron(III) are summarized in Table 6.2. The values of k'_1 , k_1 , k_2 and k_3 are of similar magnitude for Tiron and the hydroxamic acid. The fact $k_2 \gg k_1$ indicates that one

catecholate dianionic ligand or one acetohydroxamate monoanion have similar labilizing effects on substitution on aqueous iron(III). Since k_2 is of the same magnitude as k_1' , it appears that these anions have a labilizing effect similar to a hydroxide ligand. The k_3 values show that two catecholate ligands increase the reactivity by 5-10 times compared to two acetohydroxamate ligands. The dissociation rate constants (k_{-n}) are about 10^2 larger for Tiron than the acetohydroxamates, but in three systems $k_{-2} \approx 10^5 k_{-1}$ and $k_{-3} \approx 10^2 k_{-2}$.

Brink and Crumblis¹⁵ have noted an isokinetic relationship for the reactions of a series of substituted hydroxamic acids. The present values of ΔH^* and ΔS^* for k_1 , k_{-1} , k_1' and k_{-1}' seem to fit reasonably onto this isokinetic relationship.

The values of K_{cn} are more difficult to categorise because they are potentially a combination of proton release and chelate ring closing. The values decrease with increasing n as expected on simple charge arguments for either proton release or ring closure. However, there is a much larger difference between K_{c2} and K_{c3} than between K_{c1} and K_{c2} . The system can be represented by Scheme II, where $M-LH$ and $M=LH$ are the protonated monodentate and bidentate species, respectively, and $M-L$ and $M=L$ are the corresponding deprotonated species. The equilibrium constants in Scheme II

Scheme II



are related by $K_{rcH}K_{ba} = K_{ma}K_{rc}$, and the experimental K_{cn} is given by eq 6.8. If the ring closing equilibrium constants K_{rc} and K_{rcH} are much less than 1, then $K_{cn} = K_{ma}$, but if

Table 6.2. Comparison of Rate Constants for Tiron and Hydroxamate Complexes of Iron(III)

Ligand Rate Constant ^a	Tiron	Acetohydroxamic Acid ^{b,c} ($\Delta V^\ddagger$, cm ⁻³ mol ⁻¹) ^b	N-Methylacetohydroxamic Acid ^d
k_1'	1.7×10^3	5.7×10^3 ^c (5.2)	2.65×10^3
k_1	2.3	4.8 ^c (-6.3)	1.8
k_2	3.2×10^3	2.4×10^3 (-2.2)	0.81×10^3
k_3	7.7×10^3	1.6×10^3 (-2.2)	0.75×10^3
k_{-1}'	1.3	7.8×10^{-2} (-3.3)	7.1×10^{-3}
k_{-1}	1.2	7.2×10^{-2c} (-15.6)	3.2×10^{-3}
k_{-2}	$>2.8 \times 10^5$	1.3×10^3 (-9.1)	1.0×10^2
k_{-3}	1.7×10^7	9.3×10^4 (-5.4)	8.6×10^3

^a Values at 25 °C in 1.0 M NaClO₄ for Tiron and 2.0 M NaClO₄ for the hydroxamates.^b Values from ref. 4. ^c In some cases the rate constants from ref. 4 are more than 25% different from those quoted in ref. 3; in the latter, these values are $k_1' = 2 \times 10^3$, $k_1 = 1.2$, $k_{-1} = 11 \times 10^{-2}$. ^d Values from ref. 3.

$$K_{\text{cn}} = \frac{([M-L] + [M=L])[H^+]}{([M-LH] + [M= LH])} = \frac{K_{\text{ma}}(1 + K_{\text{rc}})}{1 + K_{\text{rch}}} \quad (6.8)$$

they are much larger than 1 then $K_{\text{cn}} = K_{\text{ma}}K_{\text{rc}}/K_{\text{rch}} = K_{\text{ba}}$. Another possible limiting case would assume that ring closure is very favorable for the deprotonated form, but unfavorable for the protonated form ($K_{\text{rc}} \gg 1$, $K_{\text{rch}} \ll 1$) and then $K_{\text{cn}} = K_{\text{ma}}K_{\text{rc}}$. For Tiron, the first and second acid dissociation constants are 6.8×10^{-8} and 2×10^{-12} M, respectively. The K_{cn} values are all larger than the first ionization constant of Tiron, and it seems unlikely that $K_{\text{cn}} = K_{\text{ma}}$, because this requires a $>10^7$ enhancement of the ionization of the second proton from a site somewhat remote from the metal center in the M-LH species. The only moderately analogous system of which we are aware is the salicylate complex¹⁶ of pentaamminecobalt(III) for which the -OH group has $\text{p}K_{\text{a}} = 9.77$. It seems reasonable that $\text{p}K_{\text{ma}}$ would be of this magnitude. In the same study, Liang and Gould suggest that the chelated salicylate complex $(\text{H}_2\text{O})_4\text{Cr}(\text{O}_2\text{CC}_6\text{H}_4\text{OH})^{2-}$ has $\text{p}K_{\text{a}} \approx 0.4$. This would be analogous to K_{ba} and predicts $K_{\text{ba}} \approx 0.4$ M. A similar value of ~ 0.8 M has been obtained¹⁷ for the salicylate complex $(\text{H}_2\text{O})_4\text{Fe}(\text{O}_2\text{CC}_6\text{H}_4\text{OH})^{2+}$ from the formation and dissociation kinetics. Then $K_{\text{c1}} = 0.96$ M, as obtained in this study, seems most consistent with the assignment to K_{ba} . For K_{c2} , the lower limit of >0.015 M also would seem more consistent with the assignment to K_{ba} .

The assignment of K_{c3} is much less clear cut. If one ignores the charge from the sulfonate groups in order to concentrate on the charge around the iron(III), then the protonated tris complex is either $(\text{L}=\text{O})_2\text{Fe}(\text{OH}_2)(-\text{LH})^{2-}$ or $(\text{L}=\text{O})_2\text{Fe}(=\text{LH})^{2-}$. For these species compared to $(\text{H}_2\text{O})_5\text{Fe}(-\text{LH})^{2+}$ and $(\text{H}_2\text{O})_4\text{Fe}(=\text{LH})^{2+}$, the two catecholate ligands should make ring closing less favourable in the monodentate form and H^+ dissociation less favorable in both. However, the latter effect might be small because the -OH is somewhat remote from the iron(III). In any case, it is not surprising that K_{c3}

$\ll K_{c1}$. It seems possible that the conditions leading to $K_{c3} = K_{ma}K_{rc}$ are applicable, with K_{ma} in the range of 10^{-8} to 10^{-9} , so that K_{rc} is 10^3 to 10^4 .

Experimental Section

Materials. The solutions of iron(III) perchlorate and Tiron (Eastman) were prepared as described elsewhere,¹⁴ as were the perchloric acid and sodium perchlorate.

Stopped-flow Studies. The absorbance/wavelength/time spectra (Figures 6.1–6.2) were obtained on an Applied Photophysics SQ.1 instrument. The single wavelength kinetics were studied by mixing equal volumes of solutions of iron(III) plus Tiron and perchloric acid or acetate buffer on a Tritech Dynamics Model IIA system. In this system, the storage and drive syringes, mixing and observation chambers are all submerged in a water bath to give optimum temperature uniformity. The reagent concentrations and monitoring wavelengths for the different stages are given in the Results section. Each rate constant is the average of 8 replicate determinations, evaluated by least-squares fitting to a first order rate law on a DOS 486/33 computer system interfaced to the stopped-flow system.

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Chapter 7. Kinetics of Oxidation of Iron(II)-Tiron and Iron(II)-Ascorbic Acid Solutions

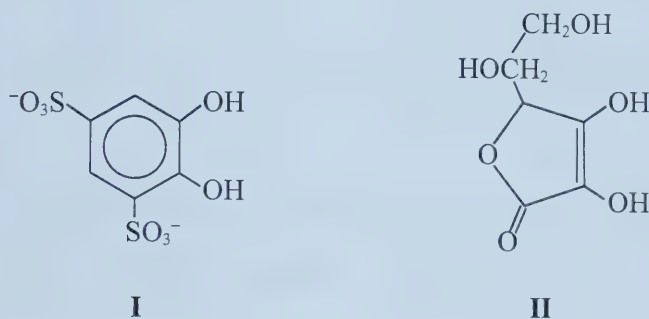
Introduction

The synthesis and study of iron(III) complexes in aqueous solution is of considerable interest because of the numerous biological functions of such systems. However such studies are limited by several features of aqueous iron(III) chemistry. The first problem is that iron(III) undergoes extensive hydrolysis and polymerization in the pH 4–7 range where many complexes of interest can be expected to form. Therefore simple mixing of aqueous iron(III) and ligand at the appropriate pH can lead to intractable mixtures. The second problem is that iron(III) is a moderately strong oxidant and oxidizes many simple organic ligands such as diols^{1–6} and thiols.^{7,8} As a result, a simple mixing process can result in destruction of the ligand.

In order to explore methods to circumvent the above problems, the present study was undertaken. The basic principle is based on the fact that aqueous iron(II) is not significantly hydrolysed at pH 7, and has no oxidizing power. If iron(II) complexes can be formed, then it may be possible to oxidize them to the desired iron(III) state. Since the iron(III) complexes would be expected to be more stable than their iron(II) parents, it may be possible to find mild oxidants that will oxidize the metal center but not affect the ligand. The present work shows that this can be done with some cobalt(III) ammine complexes and dioxygen. The kinetics of the oxidation and the solid oxidation product are studied in detail.

Results and Discussion

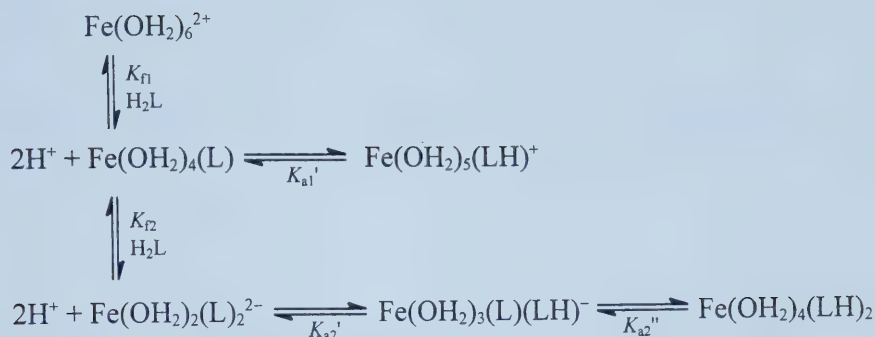
The method developed involves the rapid mixing of a solution of iron(II) and the ligands (H_2L) Tiron (**I**) or ascorbic acid (**II**) buffered at various pH values with a solution of the oxidant, also in buffer.



The iron(III)-complex products are strongly colored so that their formation can be easily monitored spectrophotometrically. The kinetics have been determined as a function of pH and the concentrations of iron(II) and ligand, with the oxidant as the deficient reagent. The standard analysis of such systems would assume that the oxidants are reacting with an equilibrium mixture of iron(II)-Tiron complexes and iron(II)-ascorbate complexes. Previous studies with other divalent first row transition metal ions indicate that the equilibria in the reactant aqueous iron(II)- H_2L system can be described by Scheme I, and the observations for Tiron, and ascorbic acid described below are consistent with this supposition.

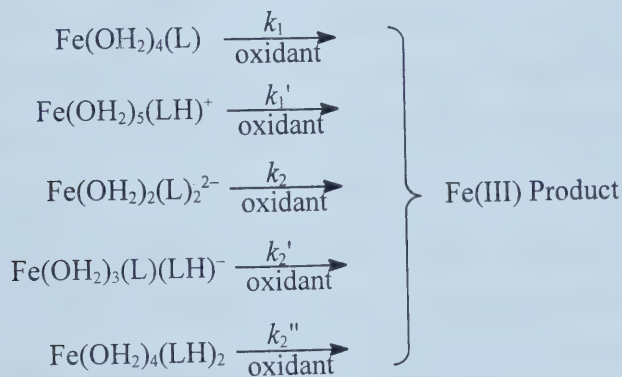
In Scheme I, it should be noted that the number of water ligands shown implies that protonated coordinated HL is monodentate, but it could be bidentate. Therefore, it is not really known whether the equilibria described by K_{a1}' , K_{a2}' and K_{a2}'' are simple

Scheme I



proton dissociations or proton dissociations plus chelation. The oxidation of these complexes can be described in general by Scheme II.

Scheme II



For the conditions $[\text{H}_2\text{L}]_{\text{tot}} > [\text{Fe(II)}] \gg [\text{oxidant}]$, if oxidation is the rate controlling step, then these Schemes predict that the pseudo-first order rate constant (k_{obsd}) is given by eq 7.1.

$$\frac{k_{\text{obsd}}}{[\text{Fe(II)}]} = \frac{(k_1'[\text{H}^+] + k_1K_{a1}')\left(\frac{K_{f1}}{K_{a1}'}\right)[\text{H}_2\text{L}] + (k_2'' + k_2'K_{a2}''[\text{H}^+]^{-1} + k_2K_{a2}'K_{a2}''[\text{H}^+]^{-2})\left(\frac{K_{f1}K_{f2}}{K_{a2}'K_{a2}''}\right)[\text{H}_2\text{L}]^2}{D} \quad (7.1)$$

where

$$D = [\text{H}^+]^2 + (K_{a1}' + [\text{H}^+])\left(\frac{K_{f1}}{K_{a1}'}\right)[\text{H}_2\text{L}] + (1 + K_{a2}''[\text{H}^+]^{-1} + K_{a2}'K_{a2}''[\text{H}^+]^{-2})\left(\frac{K_{f1}K_{f2}}{K_{a2}'K_{a2}''}\right)[\text{H}_2\text{L}]^2$$

and $[\text{H}_2\text{L}]$ is the protonated ligand concentration.

The numerator and denominator (D) of eq 7.1 are polynomials in $[\text{H}_2\text{L}]$ and $[\text{H}^+]$, and it is reasonable to expect that it will be difficult to find unique fits of the experimental k_{obsd} to this equation. At the outset it should be noted that several guiding principles have been used to obtain the best and most reasonable fit of the data. First of all, the denominator terms of eq 7.1 are independent of the nature of the oxidant and must be the same for O_2 and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. Therefore, combination of the data sets for these two oxidants may help to define the denominator terms. Secondly, it is assumed that the K_{f1} and K_{a1}' values for Fe(II) will be of similar magnitude to those for Ni(II) and Co(II), and the K_{f1} values will show the normal relationship⁹ (Irving-Williams series) of $\text{Ni(II)} > \text{Co(II)} > \text{Fe(II)}$. Finally, the k_i values extracted from the products in the numerator of eq 7.1 must be less than the diffusion controlled limit of $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Oxidation of Iron(II)–Tiron Solutions. This system was chosen because a great deal is already known about the iron(III) complexes, as reported in the previous chapter, and it is potentially simpler than ascorbic acid because Tiron is not readily oxidized by Fe(III). Furthermore, reliable equilibrium constants are available from potentiometric titrations of aqueous solutions of Tiron and Ni(II) and Co(II). These values, given in Table 7.1, provide guidance as to reasonable magnitudes for the K_{f1}

and K_{ai} values for Fe(II). The latter are not available independently, probably because of the rapid oxidation of the solutions by O_2 as described below.

The K_{f1} , K_{f2} and K_{ai} values for Fe(II) can be estimated from the Ni(II) and Co(II) values in Table 7.1. Based on the Irving-Williams series, the K_{f1} values should be in the order Ni(II) > Co(II) > Fe(II), and one can estimate for Fe(II) that $K_{f1} \approx 1 \times 10^{-11}$ M. For nickel(II) and cobalt(II), the ratios of K_{f2} to K_{f1} are 0.006 and 0.01, respectively. Therefore it seems reasonable for iron(II) that $K_{f2} \leq 0.03 \times K_{f1} \approx 3 \times 10^{-13}$, so that $K_{f1}K_{f2} \leq 3 \times 10^{-24}$. The Ni(II) and Co(II) values of K_{a1}' indicate that it should be of the order of 10^{-6} M for Fe(II). For the bis-complex, a consideration of the charge leads one to expect that $K_{a2}' \leq K_{a1}'$ and that $K_{a2}' < K_{a2}''$. A species distribution curve calculated for such values at 0.02 M total Tiron reveals that $FeLH^+$ is the dominant species from pH 4.5 to 6 but then FeL becomes significant and at pH ~ 6.5 –7 these species and the various bis complexes are making about similar contributions. For pH > 7.5, FeL_2^{2-} becomes the dominant species.

The kinetic observations can be qualitatively summarized as follows. The good exponential traces of absorbance increase with time indicate that the rate is first order in the oxidant, either $Co(NH_3)_5Cl^{2+}$ or dioxygen. The rate constant (k_{obsd}) is first order in the Fe(II) concentration (Figure 7.1) under all conditions, and increases substantially with increasing pH (Figure 7.2). The $[Tiron]^2$ dependence for O_2 (Figure 7.3) is clearly curved and indicates a saturation effect or less than second order dependence on Tiron at the higher Tiron concentrations.

The fact that the rate is first order in $[Fe(II)]$ and depends on the nature of the oxidant shows that the rate controlling step in the reaction is oxidation of the Fe(II) complexes to Fe(III) products, as assumed in the development of eq 7.1. Subsequent substitution or rearrangement of the Fe(III) complexes to the final products must be

Table 7.1. Equilibrium Constants for Aqueous M(II)-Tiron Complexes

Metal Ion	Ligand	K_{f1} , M	K_{f2} , M	K_{a1}' , M
Ni(II) ^a	Tiron	6.3×10^{-11}	4.0×10^{-13}	5.0×10^{-6}
Co(II) ^a	Tiron	2.7×10^{-11}	3.2×10^{-13}	5.2×10^{-7}
Fe(II) ^b	Tiron	$\sim 1 \times 10^{-11}$	$\sim 3 \times 10^{-13}$	$\sim 10^{-6}$
Ni(II) ^{a,c}	Ascorbate	4.0×10^{-10}		2.9×10^{-6}
Fe(II) ^a	Ascorbate	4.0×10^{-7}		2.5×10^{-3}

^a ref 9. ^b Estimated as described in text. ^c 25 °C, $\mu = 2.0$ M.

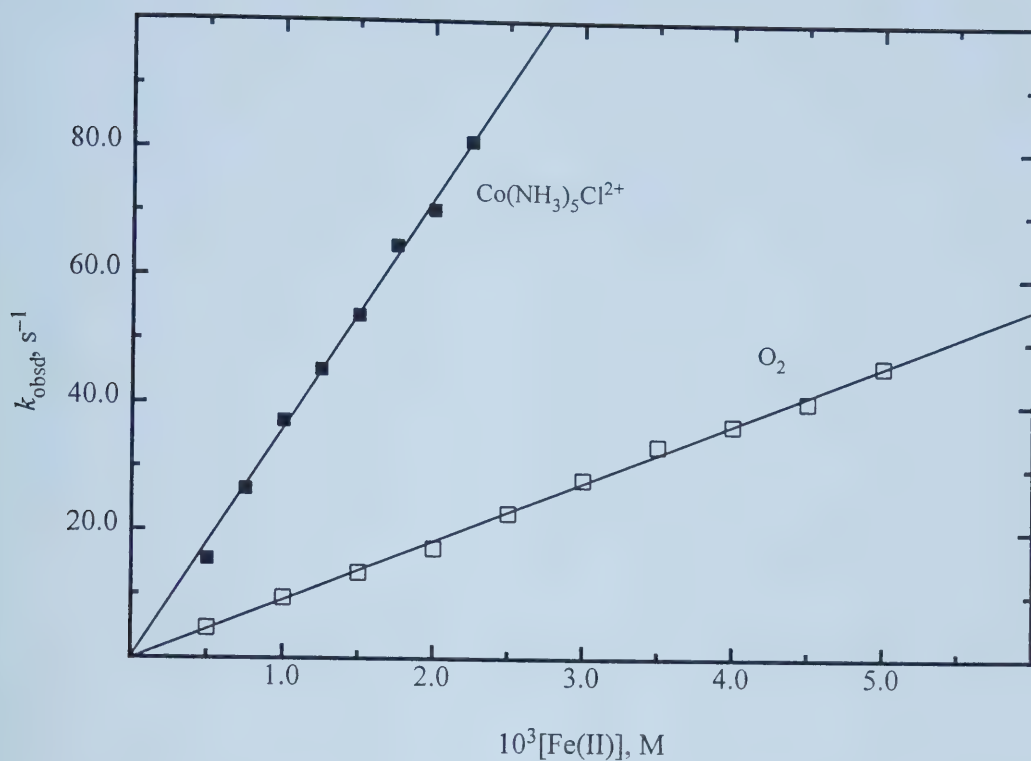


Figure 7.1. Variation of the rate constant with Fe(II) for the oxidation of Fe(II)-Tiron complexes with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ($\text{pH} = 5.49$, $[\text{Tiron}]_{\text{tot}} = 2.0 \times 10^{-2} \text{ M}$) and O_2 ($\text{pH} = 5.60$, $[\text{Tiron}]_{\text{tot}} = 4.0 \times 10^{-2} \text{ M}$) at 25°C in $1.00 \text{ M NaClO}_4/\text{HClO}_4$.

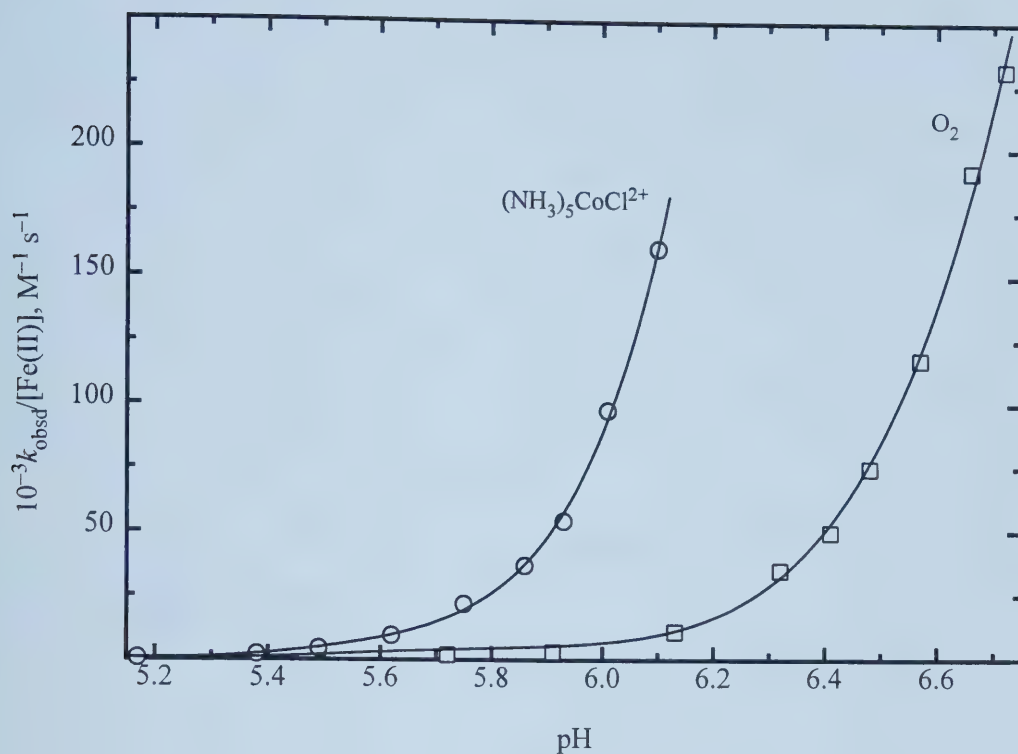


Figure 7.2. Variation of $k_{\text{obsd}}/[\text{Fe(II)}]$ with pH for the oxidation of Fe(II)-Tiron complexes ($\text{Fe(II)} = 6.0 \times 10^{-4} \text{ M}$, $[\text{Tiron}]_{\text{tot}} = 6.0 \times 10^{-3} \text{ M}$) with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and O_2 at 25°C in $1.00 \text{ M NaClO}_4/\text{HClO}_4$.

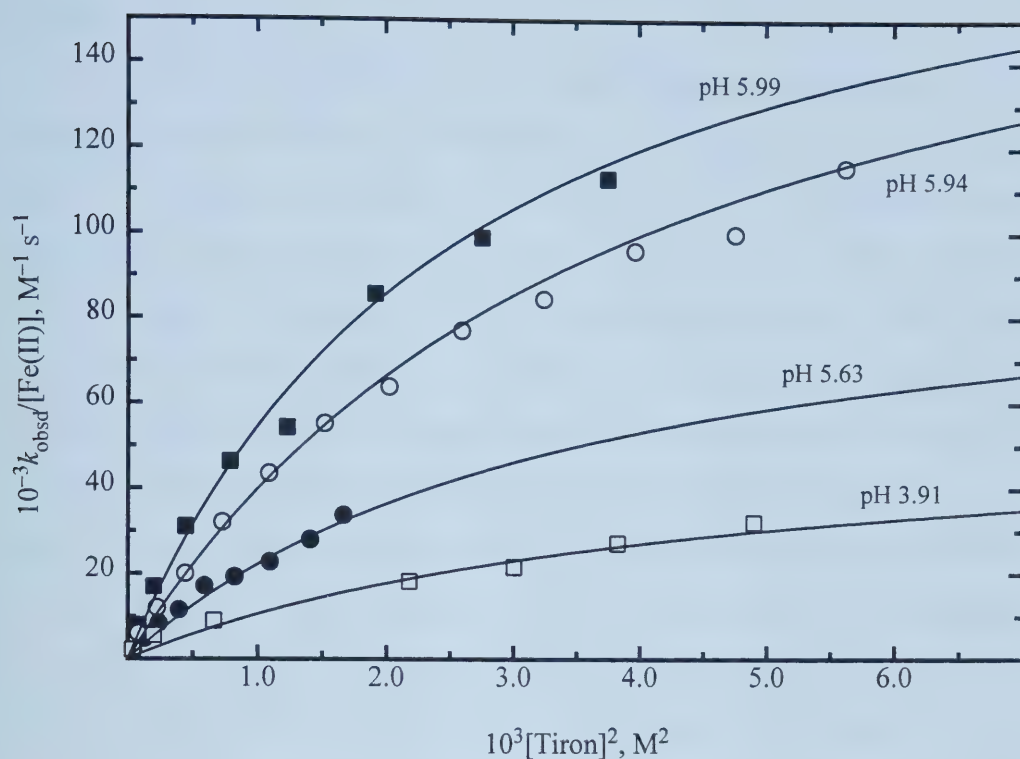


Figure 7.3. Variation of $k_{\text{obsd}}/[\text{Fe(II)}]$ with $[\text{Tiron}]^2$ for the oxidation of Fe(II)-Tiron complexes with O_2 at different pH at 25 °C in 1.00 M $\text{NaClO}_4/\text{HClO}_4$. The data at pH 5.63 and 3.91 have been multiplied by factors of 3 and 10, respectively.

fast relative to the oxidation.

To analyse the data by eq 7.1, the protonated Tiron concentration ($[H_2L]$) was calculated from the total Tiron concentration and pH using the acid dissociation constants determined by McBryde (pK_a 7.17, 11.8, $\mu = 1.0$ M).¹⁰ Preliminary least-squares fits of the experimental k_{obsd} values for each oxidant to eq 7.1, with the estimated equilibrium constants in Table 7.1, were used to determine which terms were making significant contributions. Then the data sets for both oxidants were combined and fitted to eq 7.1 to determine the kinetic coefficients in the numerator of eq 7.1 for each oxidant, and the equilibrium coefficients in the denominator of eq 7.1 that should be the same for both oxidants. The resulting values are summarized in Table 7.2, and the curves in Figures 7.1–7.3 are calculated from these parameters. Appendixes 7.1–7.2 give the complete data sets (79 conditions for O_2 , 44 conditions for $Co(NH_3)_5Cl_2^+$ and the experimental and best-fit calculated values of k_{obsd}).

The value of K_{fl} is not defined by the data, and one can only establish an upper limit of $< 2 \times 10^{-11}$ M for iron(II), based on the fact that larger values give a standard error of the fit >15 % larger than the best fit. This limit is consistent with the estimate of $K_{\text{fl}} \approx 1 \times 10^{-11}$ M for iron(II) in Table 7.1.

The value of $K_{\text{fl}}/K_{\text{al}}'$ is well defined as 8.8×10^{-5} , and the above estimate of K_{fl} gives $K_{\text{al}}' \approx 1 \times 10^{-7}$ M. This estimate for iron(II) is in the range of the values of the other M(II)-Tiron systems in Table 7.1. It is difficult to further analyse the magnitudes of K_{al}' because the reaction involved may be a mixture of complexation and proton dissociation. The analogous proton equilibria have been detected for the $Fe^{II}(\text{enterobactin})^{4-}$ system in the electrochemical study of Lee, Ecker and Raymond.¹¹ In the present terminology, since enterobactin is a tris-catecholate complex, the values of K_{a3}' , K_{a3}'' , and K_{a3}''' ($\mu = 0.4$ M) are 4×10^{-11} , 2×10^{-8} , and 1×10^{-7} M, respectively.

Table 7.2. Summary of Parameters for the Oxidation of Iron(II)–Tiron Complexes^{a,b}

Parameter	Oxidant	
	O ₂	Co(NH ₃) ₅ Cl ²⁺
$k_1'K_{f1}/K_{a1}'$	$(4.41 \pm 0.2) \times 10^{-3}$	$(3.43 \pm 0.7) \times 10^{-2}$
$k_2''K_{f1}K_{f2}/K_{a2}'K_{a2}''$		$(2.58 \pm 0.4) \times 10^{-4}$
$k_2'K_{f1}K_{f2}/K_{a2}'$	$(2.31 \pm 0.2) \times 10^{-10}$	$(4.05 \pm 0.3) \times 10^{-9}$
$k_2K_{f1}K_{f2}$	$(2.90 \pm 0.9) \times 10^{-17}$	
K_{f1}/K_{a1}'	$(9.3 \pm 1.5) \times 10^{-5}$	$(9.2 \pm 1.3) \times 10^{-5}^c$ $(8.8 \pm 2) \times 10^{-5}$
K_{f1}		$(1 \times 10^{-11})^d$
K_{f2}		$(3 \times 10^{-13})^d$
K_{a1}'		$(1.1 \times 10^{-7})^d$
K_{a2}'		$(1 \times 10^{-7})^d$
K_{a2}''		$(1 \times 10^{-7})^d$
k_1'	4.7×10	3.8×10^2
k_2''		8.6×10^5
k_2'	7.7×10^6	1.4×10^8
k_2	9.7×10^6	

^a Errors are 95 % confidence limits and are ~3.5 times larger than one standard deviation. ^b The values were determined from least-squares fitting of data from both oxidants with a fixed $K_{f1} = 1 \times 10^{-11}$ M, but the parameters change by less than half the error limit if K_{f1} is fixed between $(2-0.25) \times 10^{-11}$. ^c Determined from a fit of the combined data sets for both oxidants. ^d Estimated values used in the calculation of specific rate constant when necessary.

Lee et al.¹¹ did not comment on the large difference between K_{a3}' and K_{a3}'' , but this could reflect chelate ring opening in the first protonation.

The values of K_{a2}' and K_{a2}'' are unknown, but the kinetic results place constraints on these because the rate constants k_2' and k_2'' cannot be larger than allowed by diffusion control ($\sim 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Therefore, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ gives $k_2' = (4 \times 10^{-9} \times K_{a2}'/K_{\text{f}}K_{\text{f}2}) \leq 10^9$, and the above estimate of $K_{\text{f}}K_{\text{f}2}$ gives $K_{a2}' \leq 8 \times 10^{-7}$. Similarly, the value of $k_2''K_{\text{f}}K_{\text{f}2}/K_{a2}'K_{a2}''$ can be used to estimate that $K_{a2}'K_{a2}'' \leq 1 \times 10^{-11}$. These limits are at least consistent with the expectation from the enterobactin system and the present K_{a1}' value, that K_{a2}' and K_{a2}'' are in the range of 10^{-6} to 10^{-8} .

There are relatively few reactivity comparisons that one can make for these systems because only one specific rate constant has been defined. All of the kinetic parameters for the bis complex contain unknown equilibrium constants. It is apparent from the results in Table 7.1 that $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is about a ten fold faster oxidant for iron(II)–Tiron complexes than O_2 . If one accepts that $K_{\text{f}}K_{\text{f}2} \approx 3 \times 10^{-24}$ and that $K_{a2}' \approx K_{a2}'' \approx 1 \times 10^{-7}$, then one can estimate magnitudes of $k_2'' \approx 1 \times 10^6$, $k_2' \approx 1 \times 10^8$ for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $k_2' \approx 1 \times 10^7$ for O_2 .

Oxidation of Iron(II)–Ascorbic Acid Solutions. The ascorbic acid system also can be described by Schemes I and II. One significant difference between Tiron and ascorbic acid is that the latter is more acidic with $\text{p}K_{\text{a}}$ values of 4 and 10.9. Therefore the ascorbate ion is the dominant species under the pH conditions of this study. However, the ascorbic acid concentration (H_2L in eq 7.1) can be calculated at each pH from the total concentration and the K_{a} values, and the general equations previously given can be applied to the analysis of the ascorbic acid system. The Fe(II), pH and $[\text{ascorbate}]^2$ dependencies are shown in Figures 7.4–7.6.

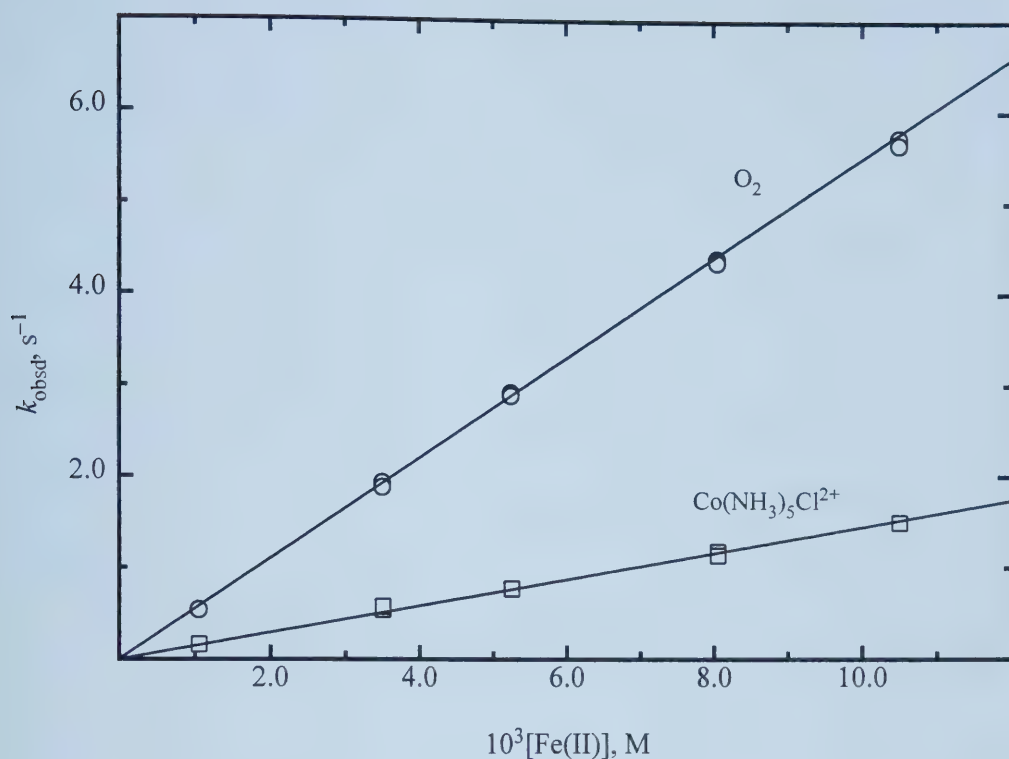


Figure 7.4. Variation of the rate constant with Fe(II) for the oxidation of Fe(II) -ascorbic acid complexes ($\text{pH} = 7.23$, $[\text{ascorbic acid}]_{\text{tot}} = 5.0 \times 10^{-2} \text{ M}$) with $\text{Co(NH}_3)_5\text{Cl}^{2+}$ and O_2 at 25°C in $1.00 \text{ M NaClO}_4/\text{HClO}_4$.

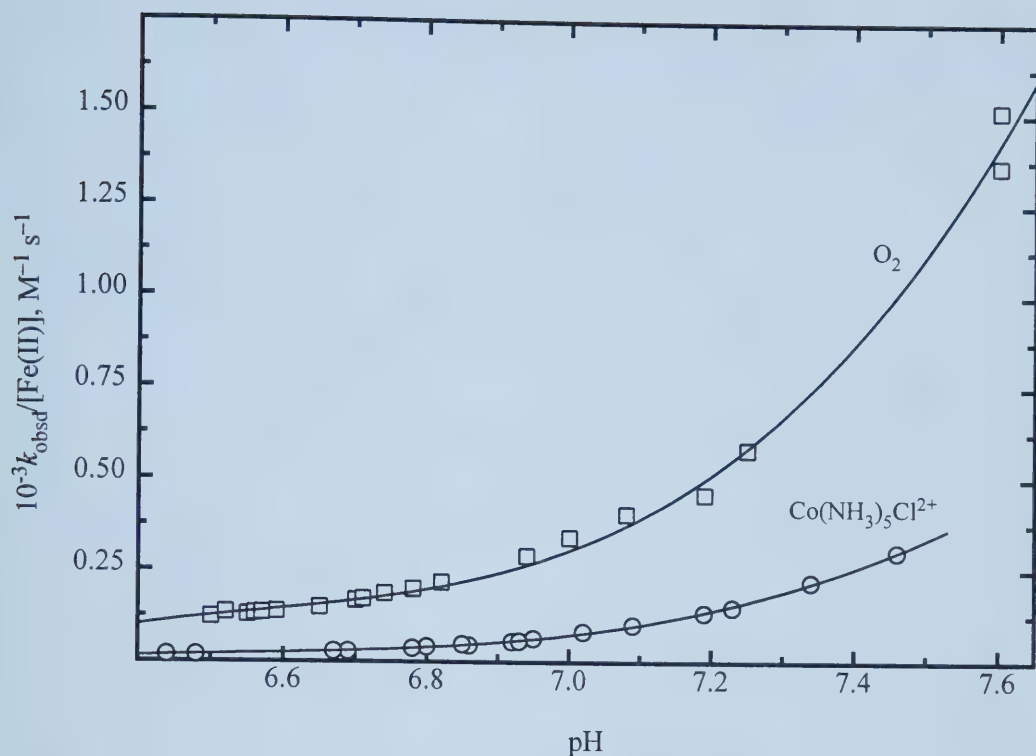


Figure 7.5. Variation of $k_{\text{obsd}}/[\text{Fe(II)}]$ with pH for the oxidation of Fe(II)-ascorbic acid complexes ($\text{Fe(II)} = 4.0 \times 10^{-3} \text{ M}$, $[\text{ascorbic acid}]_{\text{tot}} = 5.0 \times 10^{-2} \text{ M}$) with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and O_2 at 25°C in $1.00 \text{ M NaClO}_4/\text{HClO}_4$.

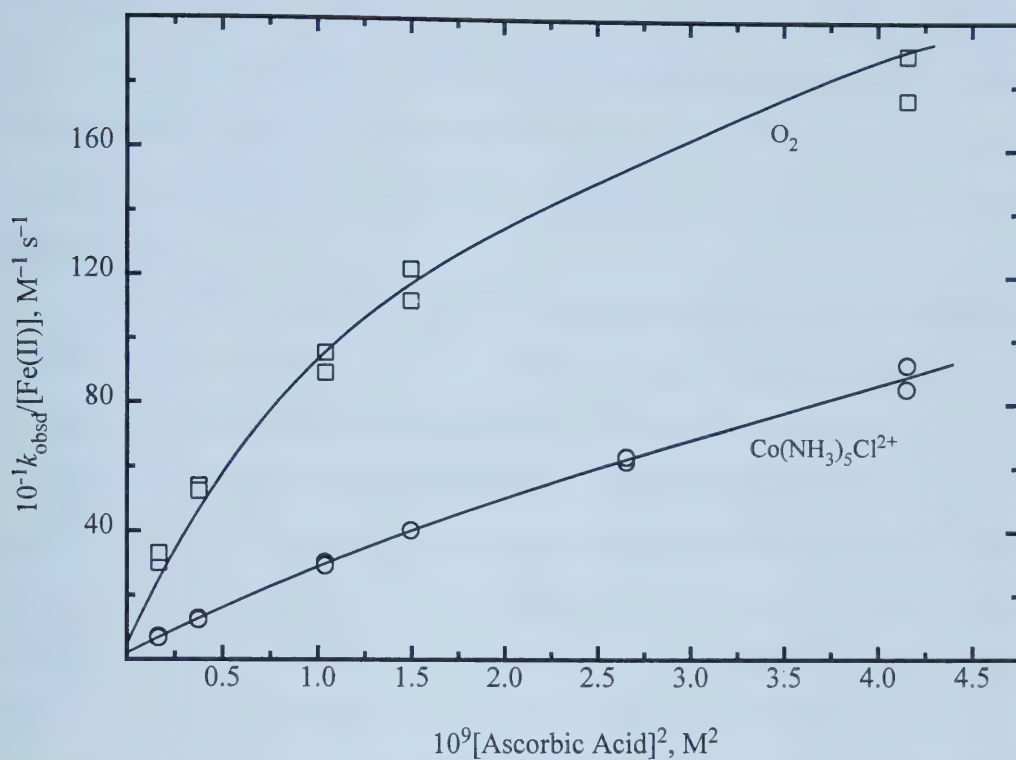


Figure 7.6. Variation of $k_{\text{obsd}}/[\text{Fe(II)}]$ with $[\text{ascorbic acid}]^2$ for the oxidation of Fe(II)-ascorbic acid complexes ($\text{pH} = 7.29$, $[\text{Fe(II)}] = 4.0 \times 10^{-3} \text{ M}$) with $\text{Co(NH}_3)_5\text{Cl}^{2+}$ and O_2 at 25°C in $1.00 \text{ M NaClO}_4/\text{HClO}_4$.

Again it should be possible to use published results to estimate the speciation terms in the denominator of eq 7.1. The available equilibrium constants for Ni(II) and Fe(II) are given in Table 7.1. The Ni(II) values appear normal relative to Tiron, but K_{fl} for Fe(II) is an unprecedented 10^3 times large than that for Ni(II), and K_{al}' also seems unusually large.

The analysis proceeded as with Tiron by determining the minimum number of parameters in the numerator of eq 7.1 that provided a satisfactory least-squares fit for each oxidant, and also gave similar values for the denominator parameters for both oxidants. The results are summarized in Table 7.3, and the full data sets are given in Appendixes 7.4–7.5. A significant difference between Tiron and ascorbic acid is that the value of $K_{\text{fl}}/K_{\text{al}}'$ is too small to be evaluated with ascorbic acid while it is well defined for Tiron. This difference is not surprising if K_{al}' is related to the ligand acidity since then one expects it to be larger for ascorbic acid, and $K_{\text{fl}}/K_{\text{al}}'$ will be correspondingly smaller. The combined least-squares fits for both oxidants give $K_{\text{fl}} = 1.8 \times 10^{-11}$ M and a lower limit for $K_{\text{al}}' \geq 2 \times 10^{-7}$ M. These can be compared to values for nickel(II) of 4.4×10^{-10} and 2.9×10^{-6} , respectively. As is normally found, K_{fl} is smaller for iron(II), and this result implies that the previously determined value (Table 7.1) is incorrect. Unfortunately, there are no values for K_{f2} for any divalent metal ions with ascorbate, but one would expect that $K_{\text{f2}} < K_{\text{fl}}$ as found with Tiron, so that probably $K_{\text{fl}}K_{\text{f2}} < 10^{-23}$.

The two oxidants show some similar reactivity with the iron(II)–ascorbate complexes, compared to the iron(II)–Tiron system. The values of $k_2K_{\text{fl}}K_{\text{f2}}$ are essentially identical for O_2 and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, with k_2 of the order of 10^5 if the above estimate of $K_{\text{fl}}K_{\text{f2}}$ is used. The oxidants differ in that O_2 shows a minor k_1' contribution, while $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ has a well defined k_2'' contribution. The results are summarized in

Table 7.3. Summary of Parameters for the Oxidation of Iron(II)–Ascorbate Complexes^{a,b}

Parameter	Oxidant	
	O ₂	Co(NH ₃) ₅ Cl ²⁺
$k_1'K_{f1}/K_{a1}'$	$(3.9 \pm 2) \times 10^{-2}$	$< 1.0 \times 10^{-2}$
k_1K_{f1}	$(6.0 \pm 0.6) \times 10^{-8}$	$(5.9 \pm 1.1) \times 10^{-9}$
$k_2''K_{f1}K_{f2}/K_{a2}'K_{a2}''$		$(2.4 \pm 0.4) \times 10^{-5}$
$k_2'K_{f1}K_{f2}/K_{a2}'$		
$k_2K_{f1}K_{f2}$	$(1.6 \pm 1.2) \times 10^{-18}$	$(1.7 \pm 0.4) \times 10^{-18}$
K_{f1}/K_{a1}'		$\leq 1 \times 10^{-4}$
K_{f1} M		$(1.8 \pm 1.5) \times 10^{-11}$
K_{f2} M		$(2 \times 10^{-13})^c$
K_{a1}' M		$(1.5 \times 10^{-6})^c$
K_{a2}' M		$(1.5 \times 10^{-6})^c$
K_{a2}'' M		$(5 \times 10^{-6})^c$
k_1' M ⁻¹ s ⁻¹	3.3×10^3	
k_1 M ⁻¹ s ⁻¹	3.3×10^3	3.3×10^2
k_2 M ⁻¹ s ⁻¹	4.5×10^5	4.7×10^5
k_2'' M ⁻¹ s ⁻¹		5.0×10^7

^a Errors are 95 % confidence limits and are ~3.8 times larger than one standard deviation. ^b The values were determined from least-squares fitting of data from both oxidants with K_{a1}' fixed at the value tabulated. ^c Estimated values used in the calculation of specific rate constant when necessary.

Table 7.3, along with the estimated equilibrium constants used to extract approximate specific rate constants from the data.

Oxidations with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. A more limited number of studies have been done on both the Tiron (11 conditions) and ascorbic acid (22 conditions) systems using $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ as the oxidizing agent. The results are consistent with the rate law found for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and the same assumptions have been used in the data analysis. The details of reaction conditions and comparison of observed and calculated rate constants are given in Appendixes 7.3 and 7.6. For Tiron the results are: $k_1'K_{\text{fl}}/K_{\text{a1}}' = (3.15 \pm 0.65) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; $k_2''K_{\text{fl}}K_{\text{f2}}/K_{\text{a2}}'K_{\text{a2}}'' = (2.33 \pm 0.42) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$; $k_2'K_{\text{fl}}K_{\text{f2}}/K_{\text{a2}}' = (3.94 \pm 0.29) \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$, with a fixed value of $K_{\text{fl}}/K_{\text{a1}}' = 9 \times 10^{-5}$ as determined from the other oxidants. For ascorbic acid, the results are: $k_1K_{\text{fl}} = (8.5 \pm 2.3) \times 10^{-9} \text{ s}^{-1}$; $k_2''K_{\text{fl}}K_{\text{f2}}/K_{\text{a2}}'K_{\text{a2}}'' = (2.1 \pm 1.0) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$; $k_2K_{\text{fl}}K_{\text{f2}} = (1.40 \pm 0.30) \times 10^{-18} \text{ M s}^{-1}$, with a fixed value of $K_{\text{fl}} = 1.8 \times 10^{-11} \text{ M}$ as determined from the other oxidants. The kinetic parameters for $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ are quite similar to those for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$.

Comparison of the Tiron and Ascorbate Systems. The Tiron and ascorbate systems are similar in that the oxidation of the bis-iron(II) complex provides the dominant pathway for oxidation. However, they differ in that the protonated Tiron complex, $\text{Fe}(\text{L})(\text{LH})^-$ is the major source for the increase in rate with increasing pH, while for ascorbate, this pH dependence is mainly due to the oxidation of $\text{Fe}(\text{L})_2^{2-}$. In both systems, the higher complexes are more rapidly oxidized. This could be attributed to their expected greater thermodynamic reducibility as the ligands increase the electron density around Fe(II) and make it more willing to release an electron to form Fe(III).

The detailed mechanism(s) for the electron transfer process cannot be directly deduced from the present observations. Since the Fe(II) complexes have water ligands

that are substitution labile, an inner-sphere mechanism is possible for both oxidants. If the reactions are outer-sphere, then Marcus' theory predicts that the ratio of the rate constants for oxidation by O_2 , $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ should be independent of the reductant. In Table 7.4, rate constants are given for oxidation of the known outer-sphere reagents $Ru(NH_3)_6^{2+}$, $Cr(bipy)_3^{2+}$ and the complexes studied here. The rate constant ratios, also given in Table 7.4, are reasonably constant for $Ru(NH_3)_6^{2+}$, $Cr(bipy)_3^{2+}$, the mono and bis ascorbate complexes and protonated mono-Tiron complex of Fe(II), and therefore seem consistent with an outer-sphere mechanism for these species. However, it must be acknowledged that this type of analysis is very qualitative and an inner-sphere mechanism is still possible.

Solid Iron(III)-Ascorbic Acid Complex. The solid iron(III)-ascorbic acid complex was synthesized by oxidizing the solutions of the iron(II) and ascorbic acid as described in the experimental section. The ion exchange behavior shows that the iron(III)-ascorbic acid complex is an anion and the atomic absorption analysis shows that sodium is the counterion. The empirical formula of the iron(III)-ascorbic acid complex is $Na_2[Fe_2(Ascorbate)_3(OH)_2] \cdot 6H_2O$. Anal. Found(calc): Fe, 13.36(13.59); C, 26.91(26.30); H, 3.86(3.92); Na, 5.35(5.59).

The solid iron(III)-ascorbate complex is very soluble in water; soluble in DMSO and methanol; insoluble in ethanol, acetone, ether, THF, 1,4-dioxane, acetonitrile and nitromethane. The maximum absorption in water at pH 6 is at 550 nm which is the same as the solution. The solid is stable in air, but the purple color of the solutions fades significantly over an hour at room temperature. The kinetic studies show that, when the solid is dissolved in 1.00 M $NaClO_4$, the rate of color disappearance is insignificantly influenced by O_2 (at pH 6.42, $k_{obsd} = 1.33 \times 10^{-3} s^{-1}$ in air and $1.40 \times 10^{-3} s^{-1}$ in argon). After reaction, iron(II) was found by adding 1,10-phenanthroline to produce the red tris-(1,10-phenanthroline)-iron(II) complex.

Table 7.4. Rate Constant Comparison with Outer-sphere Reductants

Reductant	$k, \text{M}^{-1} \text{s}^{-1}$			Ratio	
	O_2	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	$k_{\text{CoCl}}/k_{\text{O}_2}$	$k_{\text{CoBr}}/k_{\text{O}_2}$
$\text{Ru}(\text{NH}_3)_6^{2+}$	63	2.6×10^2	1.6×10^3	4.1	25
$\text{Cr}(\text{bipy})_2^{2+}$	6×10^5	8×10^5	5.0×10^6	1.3	8.3
$\text{Fe}(\text{ascorbate})$	3.3×10^3	3.3×10^2	4.7×10^2	0.1	0.14
$\text{Fe}(\text{ascorbate})_2^{2-}$	4.5×10^5	4.7×10^5	1.5×10^5	1.0	0.33
$\text{Fe}(\text{TironH})^+$	47	3.8×10^2	3.6×10^2	8.1	7.6
$\text{Fe}(\text{Tiron}_2\text{H})^-$	7.7×10^6	1.4×10^8	1.4×10^8	18	18

Earlier, Martinez et al.¹² claimed that an iron(III)-ascorbate solid was synthesized by directly mixing iron(III) and excess ascorbic acid in sodium propionate buffer. However, it is known that the iron(III) readily oxidizes ascorbic acid to produce iron(II) and dehydroascorbic acid.¹³ We found that, when iron(III) and excess ascorbic acid were mixed under anaerobic conditions, the deep purple color of the iron(III)-ascorbic acid complex did not appear and iron(II) was produced. However, exposure of this solution to air gives the same deep purple color that is observed when iron(II) in air is used as the starting material instead of iron(III).

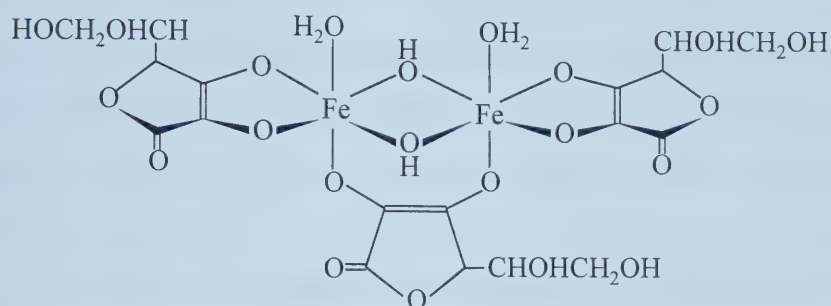
Apparently, the iron(III)-ascorbic acid complex can not be obtained by directly mixing the solutions of iron(III) and ascorbic acid unless excess ascorbic acid and some oxidant are present. Therefore, we suggest that the iron(III)-ascorbic acid complex synthesized by Martinez et al.¹² resulted from the following reactions:



We repeated Martinez's method and found that the product is the same as obtained from our procedure. It contains Fe 13.31 %, C 26.18 %, H 3.52 % and Na 5.34 % and the ion exchange behavior and sodium content show that it is an anion, not a cation as reported by Martinez et al.¹²

In the absence of a crystal structure one can only speculate on the structure of the iron(III) ascorbate anion. Probably the simplest and most symmetric ligand arrangement is shown in **III**. There are precedents for several aspects of this structure. Recently, the crystal structure of $[\text{Fe}_2\text{O}(\text{OH})(6\text{TLa})_2](\text{ClO}_4)_3$ (6TLa = tris[(6-methyl-2-pyridyl)methyl]amine) reported by Que et al.¹⁴ indicates that an oxo and a hydroxo are bridging ligands to link two iron(III). Catecholate ligands have some structural

analogy to ascorbate and have been found to bridge two metal centers as in $\text{Mo}_2(\text{Cl}_4\text{Cat})_6$,¹⁵ $\text{W}_2(\text{Cl}_4\text{Cat})_6$ ¹⁶ and $\text{Cu}_2(\text{phenoxo})(\text{Cl}_4\text{Cat})$ ¹⁷ (Cl_4Cat = tetrachlorocatecholate). Also, catecholate can have one doubly bridging oxygen and one terminal O, as found in $\text{Mn}_2(\text{DBCat})_2(\text{py})_6$, $\text{Fe}_2(\text{DBCat})_2(\text{py})_6$ and $\text{Fe}_4(\text{DBSQ})_4(\text{DBCat})_4$,^{18,19} (DBCat = 3,5-di-*tert*-butylcatecholate; DBSQ = 3,5-di-*tert*-butylsemiquinonate) so that ascorbate ligands may have these bridging modes as well.



III

Experimental Section

Materials. The solutions of iron(II) and Tiron were prepared by dissolving ferrous ammonium sulfate (BDH) and Tiron (Aldrich) at pH 3 in 1.00 M NaClO_4 , respectively. Both solutions were deoxygenated and stored under an atmosphere of purified argon. The solutions of ferrous perchlorate were prepared by dissolving ferrous perchlorate (Johnson Matthey) in the deoxygenated 1.00 M NaClO_4 . The kinetics of oxidation of ascorbic acid or Tiron with iron(II) prepared from ferrous ammonium sulfate is the same as from ferrous perchlorate and the results are shown in Appendixes 7.1 and 7.5. L-ascorbic acid (Aldrich) was dissolved in the deoxygenated 1.00 M NaClO_4 and adjusted to pH 5-6 by adding NaOH under argon condition. The

buffers used were 0.1 M MES (Aldrich), 0.1 M PIPES (Aldrich) and 0.02 M tetramethylpyrazine (Aldrich) in the range of pH 5.2-7.0, 6.0-7.5 and 3.4-4.5, respectively. The preparations of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ and $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ are described in Chapter 3.

Kinetic Measurements. All solutions were prepared freshly before the measurement. The ionic strength was adjusted to 1.00 M by $\text{NaClO}_4/\text{HClO}_4$, and the temperature was controlled at 25 ± 0.2 °C. Because all iron(II)-Tiron and iron(II)-ascorbic acid complexes are oxygen-sensitive, especially at $\text{pH} > 4$, the experiments were done under anaerobic condition by passing purified argon for at least 30 min through each solution which was protected by serum caps before mixing in one syringe.

In most cases, the concentration of ligands was 10 times larger than that of the iron(II), and the later was 10 times larger than that of the oxidants to provide pseudo-first-order condition. The typical concentration of cobalt(III) complexes was 6×10^{-5} M in the experiments. In the oxidation reaction by dioxygen, MES or PIPES buffer exposed to air was directly used if the final concentration of iron(II) was $\geq 1.0 \times 10^{-3}$ M, and the deoxygenated MES buffer was employed to give a trace amount of dioxygen if the concentration of iron(II) was $\leq 1.0 \times 10^{-3}$ M.

For the fast oxidation reaction, the experiments were performed on a Tritech Dynamics Models IIA stopped-flow spectrophotometer connected to a 486/33 computer. The mixture of iron(II) and Tiron or ascorbic acid was stored in one syringe under anaerobic conditions and then mixed with the oxidant in MES buffer at an appropriate pH in the other syringe. The $\text{pH}(\pm 0.002)$ of the reaction mixture was measured on solutions taken from the stop-syringe. The rate of appearance of iron(III)-Tiron or iron(III)-ascorbic acid complexes was followed at 480-560 nm and the

reaction rate was independent of wavelength. The recorded rate constants were the average of eight replicate determinations.

To test whether the pre-mixing time of iron(II) and ascorbic acid affects the observed rate constant, the pre-mixing time was controlled from 20 ms to 10 min before mixing with the oxidant on an Applied Photophysics SQ.1 stopped-flow instrument. The results show that the rate constant was not influenced by the pre-mixing time.

For the slower reaction ($\text{pH} < 4$), the stock solutions of Tiron (0.28M) and iron(II) (0.08M) at pH 3 NaClO_4 (1.00 M) were deoxygenated by purified argon. With syringes, appropriate volumes of Tiron and iron(II) were added to a 1 cm path length, serum capped cuvette that had been deoxygenated with argon. Then the tetramethylpyrazine buffer containing the 1×10^{-4} M deoxygenated Co(III) oxidant was added and the reactants were mixed. The absorbance was monitored at 550-560 nm on a Hewlett-Packard 8451 diode array spectrophotometer. The pH of the solution was measured after reaction. For the dioxygen oxidation, 0.9 mL of the deaerated buffer was first added to the iron(II)-Tiron solution. After mixing, the same volume of aerated buffer was added to ensure that the concentration of dioxygen was 10 times less than that of iron(II).

Preparation of Solid Iron(III)-Ascorbic Acid Complex. L-ascorbic acid (2.4 g) and MES (1.0 g) were dissolved in 45 ml of distilled water. The solution was deoxygenated by bubbling argon for about 30 min, and sodium hydroxide was added to adjust the solution to $\text{pH} \sim 7$. Then ferrous perchlorate (0.6 g) in 5 mL of distilled water under argon was added to the ascorbic acid solution. The solution was stirred for 10 min under argon and then stirred in air for about 40 min. The color of the solution changed from light brownish blue to deep purple. To this solution, 280 mL of ethanol was added with stirring and the precipitate was collected by filtration and washed with

ethanol. To purify the product, the solid was dissolved in 5 mL of distilled water and 40 mL of ethanol was added to reform the precipitate which was collected and washed twice with ethanol and once with ether. The dark purple powder (0.9 g) was stored in a vacuum desiccator protected from light by aluminium foil.

The iron in the complex was determined spectrophotometrically at 508 nm as the red iron(II) 1,10-phenanthroline complex.²⁰ Excess ascorbic acid was used as the pH 4.0 buffer and to reduce the iron(III) to iron(II). The carbon and hydrogen contents were determined in Microanalysis Laboratory in the Department of Chemistry, University of Alberta. The sodium percentages were determined by atomic absorption in Professor Cantwell's group.

To determine if the purple species is an anion or cation, an aqueous solution of the complex was loaded on anion (AG 1-X4, Cl⁻ form) and cation (Dowex 50X2-200, Na⁺ form) exchange resin, respectively. It was found that the purple solution passes through the cation exchange resin without being retained. However, it was retained on the top of the anion exchange resin. On elution with 0.1 M NaClO₄, some purple colored species was removed from the anion resin, but most was decomposed from purple to light brown color and remained on the resin during the elution. Similar elution under argon did not avoid the apparent decomposition.

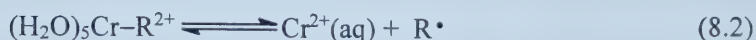
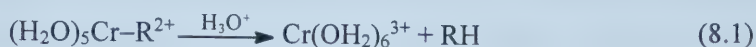
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Chapter 8. Conclusions

A large number of organochromium(III) complexes, $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$, have been synthesized and the kinetics and mechanisms of reaction have been studied. These complexes decompose in aqueous acid by heterolytic (eq 8.1) and homolytic (eq 8.2) cleavage of the chromium-carbon bond. The rates and relative importance of these processes greatly depend on the nature of the R group.¹



The substituted benzylchromium(III) complexes were chosen for study in this work for several reasons: (1) the synthesis of the complexes by bromine abstraction is a simple general method from available reagents and the complexes are stable enough to be purified under anaerobic conditions; (2) the homolysis rates for most of the benzyl derivatives are much larger than the heterolysis rate, so that homolysis and heterolysis kinetics can be studied under appropriate condition;^{2,3} (3) the Hammett constants are available for most of the benzyl species, so that the substituent effects on both homolysis and heterolysis can be established.

A large part of this work has centred on the heterolysis and homolysis kinetics of a series of the substituted benzylchromium(III) complexes. The addition of aqueous chromium(II) suppresses the homolysis in eq 8.2, and allows the heterolysis reaction to be studied as described in Chapter 2. The reaction rate of the heterolysis has terms first order and independent of $[\text{H}^+]$, e.g. $k_{\text{het}} = k_0 + k_1[\text{H}^+]$. This expression is typical for a number of organochromium(III) complexes.¹ The catalysis of the heterolysis by sulfate ion has been characterized for all but the more reactive 2-cyano and 4-cyano

systems. The catalysis by sulfate is suggested to be caused by formation of the more reactive species $(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr}-\text{R}$ as shown in Scheme I in Chapter 2. The 4-cyano system is the most reactive and is also unusual in showing a saturation effect with $[\text{H}^+]$, which is attributed to protonation of the ligand to give $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4(4-\text{CNH})^{3+}$ with $\text{p}K_{\text{a}}=1.50$. From the rate constants given in Table 2.4, there is a general trend to decreasing reactivity with increasing electron-withdrawing power of the substituent based on the Hammett σ values. This can be generally understood in terms of reduced susceptibility of the $-\text{CH}_2$ to electrophilic attack, in the absence of steric and hydrogen bonding complications involving the organic group. It also was found that the activation parameters for the uncatalysed heterolysis pathway (k_0) lie in a narrow range of 21 ± 2 for ΔH_0^* and -13.5 ± 5 for ΔS_0^* , except for the 2-cyano and 4-cyano systems.

The homolysis was studied in the presence of several oxidizing scavengers, namely, dioxygen, aqueous iron(III), $(\text{NH}_3)_5\text{CoCl}^{2+}$, and $(\text{NH}_3)_5\text{CoBr}^{2+}$, as described in Chapter 3. The homolysis rate is independent of the nature and concentration of the scavenger, as expected if homolytic cleavage is the rate-controlling step. The rate constant at 25 °C changes from 4×10^{-3} to $0.23 \times 10^{-3} \text{ s}^{-1}$ from the most reactive 4-methyl to the least reactive 3-cyano. This change is primarily due to a change in ΔH^* from 26 to 30 kcal mol^{-1} , while ΔS^* is typically in the range 22–24 $\text{cal mol}^{-1} \text{ K}^{-1}$. The Hammett relationship is found to be $\log(k_{\text{homo}}) = -2.62 - 1.06\sigma$ ($r = 0.985$) except for the 3-cyano, 3,5-difluoro and 2-cyano systems.

The correlation of the rate constants for heterolysis and homolysis of the substituted benzylchromium(III) complexes is $\log(k_{\text{homo}}) = 5.46 + 1.51 \log(k_{\text{het}})$. This implies that the strength of the Cr–C bond is important for both processes. The two exceptions to this correlation are the 2-cyano and 4-cyano complexes which undergo heterolysis faster than predicted by 10 and 50 times, respectively. The larger

heterolysis rates were attributed to delocalization of negative charge from CH_2 onto the CN substituent thereby weakening the Cr–C bond. For homolysis, this effect may be attenuated if homolysis is viewed as electron transfer from the R^- ligand to Cr(III). The electron transfer would be disfavored by delocalization.

The organic products, identified by ^1H NMR, vary considerably with the nature of the scavenger and the substituent on the benzyl ligand. With aqueous iron(III) in several systems, the products show competition between oxidation to form the alcohol and radical dimerization to give the bibenzyl derivative. From the dependence of the product distribution on the iron(III) concentration, the rate constant for oxidation of $\bullet\text{CH}_2\text{C}_6\text{H}_5$ by $\text{Fe}(\text{OH})_6^{3+}$ is calculated to be $1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. With $(\text{NH}_3)_5\text{CoBr}^{2+}$, the more easily oxidized radicals give the alcohol, while others give a mixture of alcohol and bromide or exclusively bromide for the least oxidizable systems. However, $(\text{NH}_3)_5\text{CoCl}^{2+}$ is different and gives only the bibenzyl derivative for all the systems.

As noted in Chapter 3, the reduction potential of $^+\text{CH}_2\text{C}_6\text{H}_5$ in acetonitrile has been reported as 0.73 V (vs SCE, or ~ 0.98 V vs NHE). Since $\text{Fe}(\text{OH})_6^{3+}$ with $E^0 \approx 0.75$ V is able to oxidize $\bullet\text{CH}_2\text{C}_6\text{H}_5$, this implies that the reduction potential of $^+\text{CH}_2\text{C}_6\text{H}_5$ in water must be < 0.75 V. Solvation by water may make the carbocations less reducible in water than in acetonitrile, so that the E^0 values in acetonitrile may be more positive than in water.

Chapters 4 and 5 report the heterolysis kinetics of benzyl and cyano-substituted benzyl complexes in the presence of dihydrogen phosphate/hydrogen phosphate and methyl hydrogen phosphate/methyl phosphate buffers and both heterolysis and homolysis kinetics in acetate/acetic acid buffers. The pH and total buffer dependence of the rate constants for heterolysis indicate that the conjugate bases $(\text{H}_{n-x}\text{A}^{x-})$ of the buffer species form mono complexes, $[(\text{H}_{n-x}\text{A})(\text{H}_2\text{O})_4\text{Cr}-\text{CH}_2\text{C}_6\text{H}_4\text{X}]^{2-x}$. It was found

that the formation constants (K_f) correlate with the pK_a of the parent acid ($H_{n-x+1}A^{1-x}$), according to the expression $\log(K_f) = 0.75(pK_a) - 1.76$.

In acetate buffers, the dominant heterolysis pathway involves electrophilic attack of acetic acid on the acetate complex $[(OAc)(H_2O)_4Cr-CH_2C_6H_4X]^+$ as shown in structure **I** in Chapter 5. The kinetic ambiguity for the reactions between $[(OAc)(H_2O)_4Cr-CH_2C_6H_4X]^+ + H_2O$ and $[(H_2O)_5Cr-CH_2C_6H_4X]^{2+} + OAc^-$ has been considered, and the latter pathway is favored in the present interpretation on the basis of rate constant comparisons to other systems.

The dominant factor influencing the reaction enhancement for heterolysis is the basicity of the $H_{n-x}A^{x-}$ species. A comparison of $H_{n-x}A^{x-}$ with ionizable protons and the fully deprotonated species A^{n-} reveals that the former are much more reactive than the fully deprotonated species OAc^- and $MeOPO_3^{3-}$.

For the homolysis, acetate ion causes the rate of homolysis to increase by modest factors of 1.5–2.5 for the benzyl and 3-cyano and 4-cyano systems, but causes a reduction in rate for the 2-cyano complex.

In Chapter 6, the kinetics of dissociation of the mono, bis and tris Tiron complexes with iron(III) have been studied in acidic aqueous solutions as a function of $[H^+]$ and temperature. The excellent isosbestic behavior in Figures 6.1 and 6.2 shows the clear dissociation from tris to bis and bis to mono. In general, the kinetics can be explained by two reactions, $(H_2O)Fe(L)_{n-1} + H_2L \rightleftharpoons (H_2O)Fe(L_nH) + H^+$ and $(HO)Fe(L)_{n-1} + H_2L \rightleftharpoons (H_2O)Fe(L_nH)$. The dissociation rate constants, formation rate constants and the activation parameters are summarized in Table 6.1. This study has permitted evaluation of the formation rate constants, which can not be determined directly from the simple mixing of Tiron and iron(III) because the high pH required causes extensive hydrolysis and oligomerization of aqueous iron(III).

It is shown that the formation of the mono complex from $(\text{H}_2\text{O})_5\text{Fe}(\text{OH})^{2+}$ is the dominant pathway, compared to formation from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. However, the hydrolysed species, $(\text{HO})\text{Fe}(\text{L})$ and $(\text{HO})\text{Fe}(\text{L})_2$ make little contribution to the formation of bis and tris complexes. This may be attributed to a combination of effects. The catecholate ligand reduces the charge on the iron(III) and should reduce the water ligand hydrolysis constant so that the hydrolysis species will be more minor constituents. Furthermore, the rates of substitution when one or two Tiron ligands are already present indicate that these ligands provide enough labilization so that the additional effect of an OH^- ligand is unnecessary or attenuated. From the variation in rate constants and activation parameters, it is suggested that the bis and tris complexes undergo substitution by dissociative activation, promoted by the catecholate ligands.

In Chapter 7, the kinetics of oxidation of iron(II)-Tiron and iron(II)-ascorbic acid by $(\text{NH}_3)_5\text{CoCl}^{2+}$, $(\text{NH}_3)_5\text{CoBr}^{2+}$ and O_2 has been studied at pH 3.8-7.5. The kinetic results show that the rate is first-order in iron(II) and somewhat less than second order in Tiron and ascorbic acid. The mechanism of oxidation of these complexes are described by Scheme I and II in Chapter 7. The rate controlling step in the reaction is oxidation of the iron(II) complexes to the iron(III) product, according to the dependence of the rate on the oxidants and independence of delay time of pre-mixing the solutions of iron(II) and ascorbic acid or Tiron.

Compared with the mono-iron(II) complexes, the bis-iron(II) complexes provide the significant pathway for oxidation. The major source of the increase in rate with increasing pH is the complex $\text{Fe}(\text{L})(\text{LH})^-$ for Tiron, and $\text{Fe}(\text{L})_2^{2-}$ for ascorbate. The higher reactivity of the bis complexes to the mono complexes may be attributed to the greater electron density around iron(II) that will make the iron(II) more willing to release an electron. The electron transfer mechanism for these reactions is suggested to be outer-sphere, because the ratio of the rate constants for different oxidants is fairly

independent of the reductant, and of the same magnitude as that for known outer-sphere reductants.

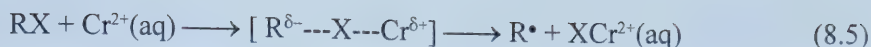
Solid iron(III)-ascorbate complex has been isolated and its properties have been studied. The empirical formula is $\text{Na}_2[\text{Fe}_2(\text{Ascorbate})_3(\text{OH})_2] \cdot 6\text{H}_2\text{O}$, according to the elemental analysis. Of the many possible structures, the one with one ascorbate ligand and two hydroxy groups linking two iron(III) ions together is favored.

Suggestions for Future Work

Effect of Substituents on Benzyl Halide Reduction by Cr(II). In our experiments, the $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complex was synthesized by mixing substituted benzyl bromides with Cr(II). It is known that the reaction takes place by bromine atom abstraction, which is the rate controlling step as shown in eq 8.3–8.4:



However, the effect of substituents, X–, on halogen atom abstraction in eq 8.3 is not yet well understood. Earlier, Kochi et al.⁴ studied the variation of the rate constants described by eq 8.3 with substituents on benzyl halides. They found that all substituents increase the rate relative to the unsubstituted compounds, whether the substituents are electron-withdrawing or electron-donating groups. Recently, Espenson et al.⁵ suggested that the halogen atom abstraction proceeds through a polar transition state, in which the developing negative charge is on the carbon from which the halogen is removed, as shown in eq 8.5. The reaction is faster in water than in alcohol

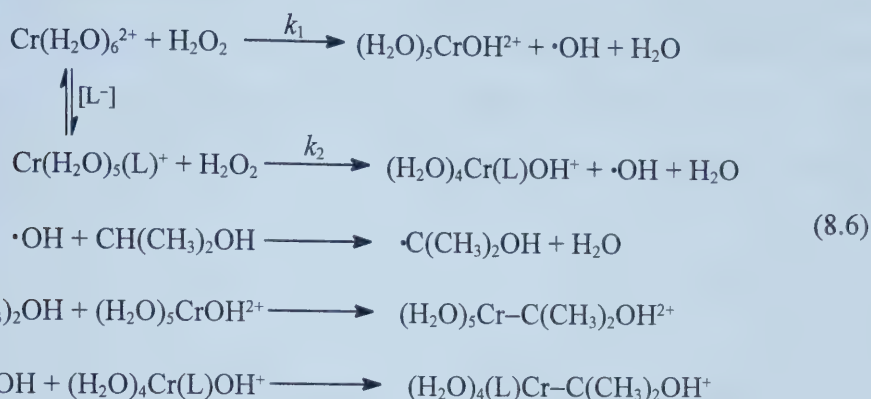


because the polar transition state is better solvated by water. Halpern et al.⁶ studied the reaction of $\text{Co}(\text{CN})_5^{3-}$ with substituted benzyl bromide and found the bromine atom abstraction rate constants in the order: $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ ($1.05 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) $>$ $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{Br}$ (7.5) $>$ $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (2.33). This trend may be extended to Cr^{2+} and is consistent with our qualitative observation that the rate at which blue chromous ion changes to the yellow-brown product is in the order $4\text{-CNC}_6\text{H}_4\text{CH}_2\text{Br} > \text{C}_6\text{H}_5\text{CH}_2\text{Br} > 4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br}$. Future work could be undertaken to measure these formation rates in water-methanol solvent mixture and quantify these substituent effects.

Measurement of the Reduction Potential of Benzyl Cation in Water. As mentioned in Chapter 3, the reduction potential of $^+\text{CH}_2\text{C}_6\text{H}_5$ in water must be less than that converted from acetonitrile medium because $\text{Fe}(\text{OH})_6^{3+}$ with $E^0 \approx 0.75 \text{ V}$ does oxidize $^+\text{CH}_2\text{C}_6\text{H}_5$ in water. In order to estimate the reduction potential of $^+\text{CH}_2\text{C}_6\text{H}_5$ in water, one might employ a series of outer-sphere oxidizing agents with known E^0 , such as the tetraamine-ruthenium(III) complexes (E^0 0.45–0.78 V),⁷ to oxidize $^+\text{CH}_2\text{C}_6\text{H}_5$. Then a lower limit on the E^0 of $^+\text{CH}_2\text{C}_6\text{H}_5$ in aqueous solution could be obtained from the organic product distributions with the different oxidants.

Effect of Anions on the Oxidation of Cr(II) by Benzyl Halides. It is known that $\text{Cr}(\text{II})$ complexed by macrocyclic ligands reacts more readily with alkyl halides due to the more negative reduction potential of these $\text{Cr}^{3+/2+}$ systems.^{8,9} However, it is not known how organic oxy anions affect the kinetics of the oxidation of $\text{Cr}(\text{II})$ by benzyl halides. Recently, van Eldik et al.¹⁰ studied the anion effect on the kinetics of the oxidation of chromium(II) by hydrogen peroxide by monitoring the formation of

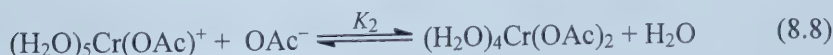
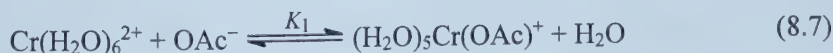
organochromium(III) products in the modified Fenton reaction as in eq 8.6. They found that all anions can accelerate the reaction by a factor of between 2 and 5



in the reactivity order $\text{CF}_3\text{COO}^- < \text{ClCH}_2\text{COO}^- \sim \text{SO}_4^{2-} \sim \text{HCOO}^- \sim \text{CH}_3\text{COO}^- \sim \text{CH}_3\text{CH}_2\text{COO}^- \sim \text{CH}_3\text{CH}(\text{OH})\text{COO}^- < \text{HOCH}_2\text{COO}^- < \text{H}_2\text{PO}_4^-$.

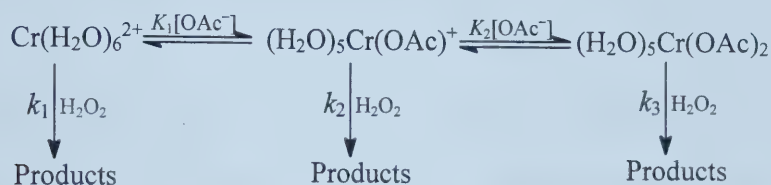
The accelerating effect of anions on the modified Fenton reaction may be due to stabilization of the positive charge that develops on chromium. From eq 8.5, an analogous process may occur during halogen atom abstraction and the donation of the negative charge by anions to Cr(II) also could stabilize the transition state.

Among all of the anions, the effect of acetate on the oxidation of Cr(II) should be studied carefully since the acetate anion is known to form several stable complexes with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ as in eq 8.7–8.9. In the modified Fenton reaction, van Eldik et al.¹⁰ found that the oxidation rate of chromium(II) by hydrogen peroxide was increased at



low acetate concentration, but then began to decrease with increasing acetate concentration. Since the dimeric species does not contribute significantly toward the acceleration effect of acetate ion on the reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with H_2O_2 ,¹¹ they presented the mechanism in Scheme I and the form of rate constant as shown in eq 8.10. From eq 8.10, they claimed that the rate constant k_3 of $(\text{H}_2\text{O})_5\text{Cr}(\text{OAc})_2$ is much smaller than k_2 of $(\text{H}_2\text{O})_5\text{Cr}(\text{OAc})^+$, in order to explain the decelerating effect of

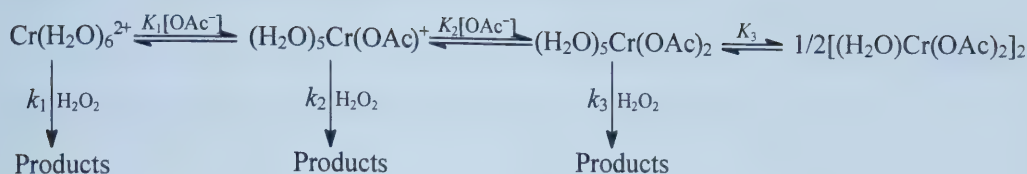
Scheme I



$$k_{\text{obsd}} = \left\{ \frac{k_1 + k_2 K_1 [\text{OAc}^-] + k_3 K_1 K_2 [\text{OAc}^-]^2}{1 + K_1 [\text{OAc}^-] + K_1 K_2 [\text{OAc}^-]^2} \right\} [\text{Cr(II)}]_{\text{total}} \quad (8.10)$$

acetate. However, it is difficult to understand why $(\text{H}_2\text{O})_5\text{Cr}(\text{OAc})_2$ is much less reactive than $(\text{H}_2\text{O})_5\text{Cr}(\text{OAc})^+$ when reacting with H_2O_2 , since two acetate ligands in $(\text{H}_2\text{O})_5\text{Cr}(\text{OAc})_2$ donate more negative charge to Cr(II) and favor the oxidation of chromium(II) by H_2O_2 . If eq 8.9 is considered, a large amount of the dimeric species $[(\text{H}_2\text{O})\text{Cr}(\text{OAc})_2]_2$ is expected to exist in the solution under the condition of high concentration of acetate because the equilibrium constant K_3 is quite large ($2.2 \times 10^4 \text{ M}^{-1}$), compared with K_1 (15 M^{-1}) and K_2 (5 M^{-1}). Therefore Scheme I should be modified to Scheme II to include the dimeric species, even though it may be less or non-reactive. The modified rate law is given in eq 8.11 in which $A = 4K_3 K_1^2 K_2^2 [\text{OAc}^-]^4$ and $B = 1 + K_1 [\text{OAc}^-] + K_1 K_2 [\text{OAc}^-]^2$.

Scheme II



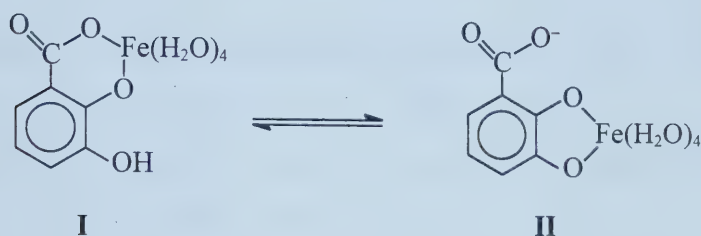
$$k_{\text{obsd}} = \left\{ \frac{k_1 + k_2 K_1 [\text{OAc}^-] + k_3 K_1 K_2 [\text{OAc}^-]^2}{A} \right\} [(B^2 + 2A[\text{Cr(II)}]_{\text{total}})^{1/2} - B] \quad (8.11)$$

From Scheme II, the decelerating effect of high concentrations of acetate could be accounted for by the decreasing concentration of monomeric species caused by the formation of a less reactive dimeric Cr(II) species.

In order to distinguish between two mechanisms, one might study the relationship between the rate constants and total concentration of chromium(II) in the presence of acetate in the halogen atom abstraction reaction. The plot of k_{obsd} vs. $[\text{Cr(II)}]_{\text{total}}$ from Scheme I should be linear, while from Scheme II, a linear plot would be obtained from k_{obsd} vs. $([\text{Cr(II)}]_{\text{total}})^{1/2}$ when $[\text{Cr(II)}]_{\text{total}} > 0.01 \text{ M}$ and $[\text{OAc}^-] > 0.1 \text{ M}$.

Kinetics of Dissociation of Fe(III) Complexes of 2,3-Dihydroxybenzoate, Salicylate and Catecholate in Aqueous Acid. The complexing and transport of Fe(III) is of considerable biological importance. Natural complexing ligands contain catechol as the active ligands and 2,3-dihydroxybenzoic acid is one such ligand. Kinetic studies have already been done for Tiron (see Chapter 6) in neutral conditions and catechol,¹² 2-hydroxybenzoic acid (salicylic acid)¹³ and 2,3-dihydroxybenzoic

acid¹⁴ in acidic conditions. It was shown that aqueous Fe(III) complexes with 2,3-dihydroxybenzoic acid in a salicylate mode (**I**) in dilute acid ($[H^+] > 0.01 \text{ M}$). However, it is possible that the complexes formed (**I**) will rearrange to the catecholate form (**II**) under neutral conditions because higher pH (which is closer to biological conditions) promotes the release of a proton from the -OH group.



Jordan and Li¹⁵ studied the kinetics and mechanism of the nickel(II)-2,3-dihydroxybenzoate system near pH 7 and observed interconversion of the two linkage isomers with nickel(II). The presence of such an interconversion with iron(III) might be uncovered by a study of the dissociation of Fe(III)-2,3-dihydroxybenzoate complexes in aqueous acid, as described in Chapter 6 for Fe(III)-Tiron complexes. For comparison, the kinetics of dissociation of Fe(III)-salicylate and Fe(III)-catecholate complexes also should be undertaken.

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Appendix. Tables of Data and Derivations of Equations

Appendix 2.1. Rate Constants for the Heterolysis of 4-Methylbenzylpentaqua-chromium(III) Observed at 362 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺] M ^a	10 ² × [SO ₄ ²⁻] _t M ^b	10 ⁴ × <i>k</i> , s ⁻¹	
			Obsd.	Calcd.
59.1	0.0150	6.390	3.72	3.69
59.1	0.0334	6.390	3.63	3.54
59.1	0.0610	6.390	3.43	3.37
59.1	0.100	6.390	3.30	3.22
59.1	0.236	6.390	3.11	3.08
59.1	0.328	6.390	3.09	3.10
59.1	0.420	6.390	3.17	3.14
59.1	0.558	6.390	3.22	3.22
59.1	0.696	6.390	3.36	3.31
59.1	0.925	6.390	3.49	3.48
59.1	0.100	0.915	2.32	2.33
59.1	0.100	3.645	2.83	2.75
59.1	0.100	9.135	3.72	3.73
67.3	0.0150	6.390	7.88	8.12
67.3	0.0334	6.390	7.32	7.66
67.3	0.0610	6.390	6.96	7.14
67.3	0.100	6.390	6.65	6.68
67.3	0.236	6.390	6.21	6.26
67.3	0.328	6.390	6.12	6.26

67.3	0.428	6.390	6.15	6.31
67.3	0.558	6.390	6.34	6.42
67.3	0.742	6.390	6.54	6.61
67.3	0.925	6.390	6.73	6.81
67.3	0.100	0.915	4.58	4.76
67.3	0.100	3.645	5.70	5.65
67.3	0.100	9.135	7.52	7.86
74.2	0.015	6.390	15.6	15.4
74.2	0.024	6.390	14.4	14.8
74.2	0.144	6.390	11.7	11.5
74.2	0.236	6.390	11.0	11.1
74.2	0.328	6.390	11.0	11.0
74.2	0.558	6.390	11.3	11.2
74.2	0.742	6.390	11.7	11.5
74.2	0.925	6.390	12.0	11.8
74.2	0.0128	3.645	12.7	12.1
74.2	0.0317	3.645	11.5	11.3
74.2	0.0600	3.645	10.9	10.6
74.2	0.145	3.645	9.82	9.89
74.2	0.239	3.645	9.84	9.81
74.2	0.334	3.645	9.78	9.87
74.2	0.570	3.645	10.2	10.2
74.2	0.758	3.645	10.6	10.5
74.2	0.947	3.645	10.7	10.8
74.2	0.100	0.915	8.29	8.47
74.2	0.100	1.830	8.82	8.99

74.2	0.100	3.645	10.1	10.1
74.2	0.100	6.390	12.3	12.0
74.2	0.100	9.135	14.2	14.3
74.2	0.0400	0.915	8.43	8.56
74.2	0.0400	1.830	9.61	9.32
74.2	0.0400	3.645	11.2	11.0
74.2	0.0400	5.025	12.7	12.5
74.2	0.0400	6.390	13.9	14.0

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.2. Rate Constants for the Heterolysis of Benzylpentaquachromium(III)Observed at 356 nm in 1.00 M HClO₄/NaClO₄

Temp	[H ⁺]	10 ² × [SO ₄ ²⁻] _i	10 ⁴ × <i>k</i> , s ⁻¹	
°C	M ^a	M ^b	Obsd.	Calcd.
59.3	0.0150	6.390	3.04	3.06
59.3	0.0334	6.390	2.98	2.93
59.3	0.0610	6.390	2.92	2.79
59.3	0.236	6.390	2.63	2.58
59.3	0.328	6.390	2.62	2.62
59.3	0.558	6.390	2.68	2.76
59.3	0.696	6.390	2.85	2.87
59.3	0.834	6.390	2.96	2.97
59.3	0.925	6.390	3.09	3.05
59.3	0.100	0.915	1.85	1.78
59.3	0.100	3.645	2.27	2.20
59.3	0.100	6.390	2.69	2.67
59.3	0.100	9.135	3.11	3.17
67.3	0.0150	6.390	6.59	6.72
67.3	0.0242	6.390	6.41	6.53
67.3	0.0426	6.390	5.96	6.19
67.3	0.0610	6.390	5.92	5.92
67.3	0.144	6.390	5.33	5.35
67.3	0.236	6.390	5.12	5.22
67.3	0.328	6.390	5.18	5.23
67.3	0.558	6.390	5.48	5.40

67.3	0.696	6.390	5.55	5.53
67.3	0.834	6.390	5.67	5.68
67.3	0.925	6.390	5.72	5.78
67.3	0.100	3.645	4.59	4.63
67.3	0.100	6.390	5.71	5.55
67.3	0.100	9.135	6.48	6.59
67.3	0.0128	0.0 ^c	3.33	3.46
67.3	0.100	0.0 ^c	3.39	3.57
67.3	0.334	0.0 ^c	3.81	3.84
67.3	0.570	0.0 ^c	4.12	4.12
67.3	0.711	0.0 ^c	4.38	4.28
67.3	0.934	0.0 ^c	4.58	4.54
74.3	0.0150	6.390	13.3	13.0
74.3	0.0242	6.390	12.2	12.6
74.3	0.0400	6.390	11.5	11.9
74.3	0.0610	6.390	11.3	11.1
74.3	0.236	6.390	9.45	9.51
74.3	0.328	6.390	9.51	9.46
74.3	0.558	6.390	9.66	9.63
74.3	0.696	6.390	9.88	9.80
74.3	0.834	6.390	10.0	9.98
74.3	0.925	6.390	10.2	10.1
74.3	0.0128	3.645	10.4	10.3
74.3	0.0223	3.645	10.3	9.92
74.3	0.0400	3.645	9.66	9.41
74.3	0.0600	3.645	9.12	9.03
74.3	0.239	3.645	8.27	8.43

74.3	0.334	3.645	8.17	8.49
74.3	0.570	3.645	8.62	8.76
74.3	0.711	3.645	9.02	8.95
74.3	0.853	3.645	9.07	9.15
74.3	0.947	3.645	9.28	9.29
74.3	0.100	0.915	7.48	7.28
74.3	0.100	0.915 ^d	7.22	7.28
74.3	0.100	3.645	8.94	8.65
74.3	0.100	3.645 ^d	9.04	8.65
74.3	0.100	3.645 ^e	9.15	8.65
74.3	0.100	6.390	10.5	10.27
74.3	0.100	7.755	11.3	11.2
74.3	0.100	7.755 ^e	11.4	11.2
74.3	0.100	9.135	12.1	12.2
74.3	0.100	9.135 ^d	12.2	12.2
74.3	0.0400	0.915	7.50	7.35

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated. ^c In 0.0426 M Cr(II) derived from reduction of $\text{Cr}(\text{ClO}_4)_3$. ^d In 0.0426 M Cr(II) derived from reduction of $\text{Cr}(\text{ClO}_4)_3$, with sulfate ion from ZnSO_4 . ^e In 0.0426 M Cr(II) derived from reduction of $\text{Cr}(\text{ClO}_4)_3$, with sulfate ion from Na_2SO_4 .

Appendix 2.3. Rate Constants for the Heterolysis of 4-Fluorobenzylpenta-aquachromium(III) Observed at 354 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺]	10 ² × [SO ₄ ²⁻] _t	10 ⁴ × <i>k</i> , s ⁻¹	
	M ^a	M ^b	Obsd.	Calcd.
59.0	0.0129	3.705	2.44	2.44
59.0	0.0317	3.705	2.36	2.33
59.0	0.0600	3.705	2.25	2.23
59.0	0.100	3.705	2.14	2.15
59.0	0.239	3.705	2.11	2.11
59.0	0.335	3.705	2.15	2.14
59.0	0.569	3.705	2.22	2.23
59.0	0.761	3.705	2.33	2.33
59.0	0.100	0.930	1.75	1.75
59.0	0.100	1.860	1.87	1.88
59.0	0.100	3.705	2.17	2.15
59.0	0.100	4.635	2.28	2.30
66.8	0.0129	3.705	5.57	5.57
66.8	0.0317	3.705	5.09	5.18
66.8	0.0600	3.705	4.46	4.81
66.8	0.100	3.705	4.52	4.56
66.8	0.146	3.705	4.43	4.44
66.8	0.239	3.705	4.33	4.38
66.8	0.335	3.705	4.45	4.40
66.8	0.569	3.705	4.52	4.56
66.8	0.761	3.705	4.72	4.72

66.8	0.950	3.705	4.92	4.90
66.8	0.100	0.930	3.65	3.67
66.8	0.100	1.860	3.93	3.95
66.8	0.100	2.790	4.33	4.25
66.8	0.100	3.705	4.52	4.56
66.8	0.100	4.635	4.97	4.89
74.0	0.0400	0.930	7.30	7.24
74.0	0.0400	1.860	8.24	8.13
74.0	0.0400	2.790	9.10	9.11
74.0	0.0400	3.705	10.40	10.17
74.0	0.0400	4.635	10.75	11.32
74.0	0.100	0.960	6.91	7.08
74.0	0.100	1.860	7.46	7.62
74.0	0.100	2.790	8.04	8.00
74.0	0.100	3.240	8.64	8.52
74.0	0.100	4.635	9.52	9.53
74.0	0.0114	1.860	9.51	8.97
74.0	0.0211	1.860	8.88	8.59
74.0	0.0403	1.860	8.24	8.12
74.0	0.0789	1.860	7.79	7.72
74.0	0.146	1.860	7.44	7.53
74.0	0.243	1.860	7.44	7.55
74.0	0.339	1.860	7.49	7.64
74.0	0.580	1.860	7.93	7.98
74.0	0.905	1.860	8.47	8.49
74.0	0.0128	3.705	11.38	11.67

74.0	0.0319	3.705	10.45	10.53
74.0	0.0605	3.705	9.88	9.50
74.0	0.146	3.705	8.73	8.52
74.0	0.241	3.705	8.17	8.33
74.0	0.336	3.705	8.28	8.34
74.0	0.574	3.705	8.67	8.59
74.0	0.764	3.705	9.01	8.86
74.0	0.954	3.705	9.24	9.12

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.4. Rate Constants for the Heterolysis of 2,4-Difluorobenzylpenta-aqua-chromium(III) Observed at 350 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺]	10 ² × [SO ₄ ²⁻] _i	10 ⁴ × <i>k</i> , s ⁻¹	
	M ^a	M ^b	Obsd.	Calcd.
64.0	0.0149	6.210	2.64	2.65
64.0	0.0334	6.210	2.50	2.49
64.0	0.0611	6.210	2.31	2.30
64.0	0.100	6.210	2.14	2.14
64.0	0.237	6.210	1.97	1.97
64.0	0.329	6.210	1.95	1.95
64.0	0.561	6.210	1.98	1.98
64.0	0.746	6.210	1.97	2.02
64.0	0.930	6.210	2.11	2.06
64.0	0.100	1.860	1.59	1.59
64.0	0.100	3.705	1.88	1.81
64.0	0.100	9.270	2.54	2.60
69.0	0.0149	6.210	4.62	4.59
69.0	0.0241	6.210	4.26	4.41
69.0	0.0426	6.210	4.08	4.10
69.0	0.0611	6.210	3.93	3.84
69.0	0.100	6.210	3.54	3.50
69.0	0.237	6.210	3.11	3.14
69.0	0.329	6.210	3.03	3.09
69.0	0.561	6.210	3.10	3.09
69.0	0.746	6.210	3.16	3.13

69.0	0.930	6.210	3.14	3.18
69.0	0.100	1.860	2.54	2.62
69.0	0.100	3.705	2.92	2.96
69.0	0.100	7.890	3.94	3.92
69.0	0.100	9.270	4.38	4.29
74.0	0.0130	3.705	6.67	6.18
74.0	0.0224	3.705	6.28	5.89
74.0	0.0318	3.705	5.87	5.64
74.0	0.0603	3.705	5.41	5.13
74.0	0.100	3.705	4.86	4.80
74.0	0.240	3.705	4.40	4.50
74.0	0.335	3.705	4.30	4.46
74.0	0.572	3.705	4.39	4.49
74.0	0.761	3.705	4.50	4.55
74.0	0.950	3.705	4.59	4.61
74.0	0.015	6.210	7.95	7.87
74.0	0.024	6.210	7.09	7.50
74.0	0.033	6.210	7.03	7.16
74.0	0.061	6.210	6.60	6.35
74.0	0.100	6.210	5.70	5.67
74.0	0.237	6.210	5.06	4.98
74.0	0.329	6.210	4.91	4.87
74.0	0.561	6.210	4.87	4.83
74.0	0.746	6.210	4.91	4.86
74.0	0.930	6.210	5.11	4.91
74.0	0.100	9.270	6.67	7.00

74.0	0.100	1.860	4.21	4.26
74.0	0.0400	0.930	4.14	4.13
74.0	0.0400	3.705	5.40	5.46
74.0	0.0400	6.210	6.72	6.94
74.0	0.0400	1.860	4.43	4.53
74.0	0.0400	5.100	6.09	6.26

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.5. Rate Constants for the Heterolysis of 3,5-Difluorobenzylpenta-aqua-chromium(III) Observed at 348 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺]	10 ² × [SO ₄ ²⁻] _t	10 ⁴ × <i>k</i> , s ⁻¹	
	M ^a	M ^b	Obsd.	Calcd.
64.0	0.0149	6.210	2.12	2.01
64.0	0.0334	6.210	1.88	1.89
64.0	0.0611	6.210	1.73	1.76
64.0	0.100	6.210	1.64	1.65
64.0	0.144	6.210	1.60	1.59
64.0	0.237	6.210	1.56	1.58
64.0	0.329	6.210	1.66	1.61
64.0	0.561	6.210	1.76	1.74
64.0	0.746	6.210	1.86	1.85
64.0	0.930	6.210	1.93	1.98
64.0	0.100	1.860	1.15	1.15
64.0	0.100	3.705	1.34	1.35
64.0	0.100	7.890	1.89	1.87
69.0	0.0149	6.210	3.53	3.51
69.0	0.0241	6.210	3.36	3.39
69.0	0.0334	6.210	3.16	3.28
69.0	0.0611	6.210	2.93	3.02
69.0	0.100	6.210	2.87	2.81
69.0	0.237	6.210	2.62	2.64
69.0	0.329	6.210	2.69	2.67
69.0	0.561	6.210	2.85	2.82

69.0	0.746	6.210	2.94	2.97
69.0	0.930	6.210	3.18	3.13
69.0	0.100	1.860	1.88	1.89
69.0	0.100	3.705	2.31	2.26
69.0	0.100	7.890	3.10	3.21
69.0	0.100	9.270	3.53	3.56
74.0	0.0130	3.705	4.71	4.55
74.0	0.0224	3.705	4.53	4.37
74.0	0.0318	3.705	4.29	4.22
74.0	0.0603	3.705	4.04	3.91
74.0	0.100	3.705	3.77	3.73
74.0	0.144	3.705	3.49	3.66
74.0	0.240	3.705	3.54	3.66
74.0	0.335	3.705	3.59	3.72
74.0	0.572	3.705	3.77	3.95
74.0	0.761	3.705	4.13	4.15
74.0	0.950	3.705	4.40	4.36
74.0	0.015	6.210	6.18	6.07
74.0	0.024	6.210	5.84	5.84
74.0	0.033	6.210	5.61	5.63
74.0	0.061	6.210	5.28	5.13
74.0	0.100	6.210	4.81	4.73
74.0	0.144	6.210	4.66	4.53
74.0	0.237	6.210	4.47	4.41
74.0	0.329	6.210	4.49	4.42
74.0	0.561	6.210	4.59	4.60

74.0	0.746	6.210	4.85	4.78
74.0	0.930	6.210	5.14	4.98
74.0	0.100	0.930	2.73	2.74
74.0	0.100	3.705	3.77	3.73
74.0	0.100	5.565	4.56	4.46
74.0	0.100	6.210	4.81	4.73
74.0	0.100	7.230	5.17	5.17
74.0	0.100	9.270	5.90	6.11
74.0	0.0400	0.930	2.82	2.75
74.0	0.0400	2.790	3.52	3.63
74.0	0.0400	3.705	4.09	4.11
74.0	0.0400	4.635	4.60	4.61
74.0	0.0400	6.210	5.16	5.49

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.6. Rate Constants for the Heterolysis of 3-Cyanobenzylpentaqua-chromium(III) Observed at 310 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺]	10 ² × [SO ₄ ²⁻] _i	10 ⁴ × <i>k</i> , s ⁻¹	
	M ^a	M ^b	Obsd.	Calcd.
64.0	0.0149	6.210	2.20	2.16
64.0	0.0334	6.210	2.06	2.05
64.0	0.0611	6.210	1.93	1.93
64.0	0.100	6.210	1.86	1.82
64.0	0.146	6.210	1.79	1.77
64.0	0.237	6.210	1.75	1.73
64.0	0.329	6.210	1.72	1.74
64.0	0.561	6.210	1.82	1.81
64.0	0.746	6.210	1.88	1.87
64.0	0.930	6.210	1.95	1.94
64.0	0.100	1.860	1.24	1.24
64.0	0.100	3.705	1.52	1.48
64.0	0.100	9.270	2.24	2.28
69.0	0.0149	6.210	3.89	3.75
69.0	0.0241	6.210	3.44	3.63
69.0	0.0400	6.210	3.41	3.43
69.0	0.0611	6.210	3.13	3.23
69.0	0.100	6.210	3.04	3.01
69.0	0.237	6.210	2.77	2.79
69.0	0.329	6.210	2.77	2.79
69.0	0.561	6.210	2.83	2.86

69.0	0.746	6.210	2.92	2.95
69.0	0.930	6.210	3.05	3.05
69.0	0.100	1.860	1.98	2.05
69.0	0.100	3.705	2.47	2.43
69.0	0.100	7.890	3.31	3.42
69.0	0.100	9.270	3.84	3.79
74.0	0.0129	3.705	5.17	4.90
74.0	0.0224	3.705	4.87	4.69
74.0	0.0318	3.705	4.67	4.52
74.0	0.146	3.705	3.74	3.85
74.0	0.240	3.705	3.63	3.80
74.0	0.335	3.705	3.75	3.82
74.0	0.572	3.705	3.89	3.95
74.0	0.761	3.705	4.10	4.09
74.0	0.950	3.705	4.20	4.22
74.0	0.015	6.210	6.26	6.41
74.0	0.024	6.210	6.16	6.15
74.0	0.033	6.210	5.70	5.91
74.0	0.061	6.210	5.28	5.34
74.0	0.144	6.210	4.73	4.62
74.0	0.237	6.210	4.44	4.45
74.0	0.329	6.210	4.53	4.42
74.0	0.561	6.210	4.60	4.50
74.0	0.746	6.210	4.77	4.61
74.0	0.930	6.210	4.74	4.74
74.0	0.100	1.860	3.40	3.34

74.0	0.100	3.705	4.05	3.95
74.0	0.100	7.890	5.51	5.57
74.0	0.100	6.210	5.04	4.88
74.0	0.100	9.270	6.03	6.19
74.0	0.0400	0.930	2.98	3.10
74.0	0.0400	1.860	3.53	3.50
74.0	0.0400	3.705	4.49	4.39
74.0	0.0400	5.100	5.39	5.14
74.0	0.0400	6.210	5.57	5.75

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.7. Rate Constants for the Heterolysis of 4-Cyanobenzylpenta-aqua-chromium(III) Observed at 310 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺]	10 ² × [SO ₄ ²⁻] _t	10 ⁴ × <i>k</i> , s ⁻¹	
	M ^a	M ^b	Obsd.	Calcd.
25.0	0.0111	1.500	0.974	0.994
25.0	0.0305	1.500	1.35	1.34
25.0	0.0595	1.500	1.60	1.59
25.0	0.0981	1.500	1.73	1.76
25.0	0.243	1.500	1.88	1.97
25.0	0.337	1.500	1.96	2.02
25.0	0.582	1.500	2.08	2.07
25.0	0.775	1.500	2.10	2.09
25.0	0.968	1.500	2.18	2.10
35.0	0.0111	1.500	2.91	2.91
35.0	0.0208	1.500	3.83	3.74
35.0	0.0401	1.500	5.02	4.89
35.0	0.0595	1.500	5.77	5.65
35.0	0.0981	1.500	6.50	6.57
35.0	0.147	1.500	7.04	7.20
35.0	0.243	1.500	7.56	7.82
35.0	0.337	1.500	7.91	8.12
35.0	0.582	1.500	8.42	8.47
35.0	0.775	1.500	8.75	8.60
35.0	0.968	1.500	8.80	8.68
43.0	0.0111	1.500	6.29	6.46

43.0	0.0208	1.500	8.70	8.68
43.0	0.0305	1.500	10.6	10.5
43.0	0.0401	1.500	12.1	12.0
43.0	0.0595	1.500	14.1	14.4
43.0	0.0788	1.500	15.6	16.1
43.0	0.0981	1.500	17.5	17.5
43.0	0.147	1.500	19.1	19.7
43.0	0.243	1.500	21.4	21.9
43.0	0.337	1.500	22.7	23.1
43.0	0.582	1.500	24.7	24.4
43.0	0.775	1.500	25.3	24.9
43.0	0.968	1.500	25.6	25.2

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

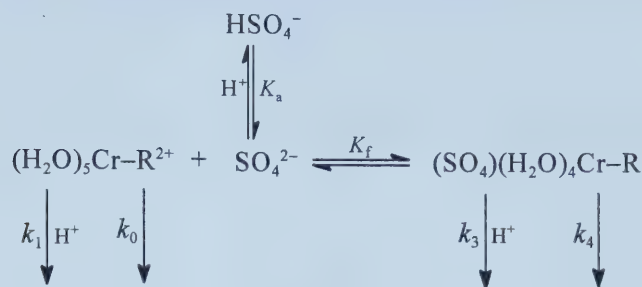
Appendix 2.8. Rate Constants for the Heterolysis of 2-Cyanobenzylpentaqua-chromium(III) Observed at 316 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺] M ^a	10 ² × [SO ₄ ²⁻] _i M ^b	10 ⁴ × <i>k</i> , s ⁻¹	
			Obsd.	Calcd.
57.0	0.0129	3.675	6.54	6.72
57.0	0.0319	3.675	6.72	6.74
57.0	0.0600	3.675	6.66	6.76
57.0	0.0985	3.675	6.69	6.81
57.0	0.146	3.675	6.85	6.86
57.0	0.241	3.675	7.09	6.97
57.0	0.241	3.675	7.04	6.97
57.0	0.336	3.675	7.03	7.09
57.0	0.574	3.675	7.32	7.39
57.0	0.765	3.675	7.51	7.62
57.0	0.955	3.675	7.72	7.86
64.0	0.0129	3.705	14.0	14.1
64.0	0.0416	3.705	14.1	14.1
64.0	0.100	3.705	14.3	14.3
64.0	0.243	3.705	14.8	14.7
64.0	0.338	3.705	15.2	14.9
64.0	0.338	3.705	15.6	14.9
64.0	0.578	3.705	15.9	15.6
64.0	0.769	3.705	16.6	16.2
64.0	0.100	6.480	14.6	14.2
64.0	0.100	9.255	14.6	14.2

64.0	0.100	1.845	14.6	14.3
74.0	0.0129	3.675	37.5	38.4
74.0	0.0414	3.675	38.2	38.5
74.0	0.0985	3.675	37.9	39.0
74.0	0.241	3.675	39.7	40.2
74.0	0.241	3.675	41.1	40.2
74.0	0.336	3.675	41.1	41.1
74.0	0.574	3.675	43.9	43.3
74.0	0.765	3.675	45.5	45.0
74.0	0.954	3.675	45.9	46.8
74.0	0.954	3.675	45.9	46.8

^a This is the total HClO_4 concentration added, and was corrected for HSO_4^- formed to obtain the equilibrium H^+ concentration. ^b The sulfate is derived from $\text{Cr}_2(\text{SO}_4)_3$, and is 1.5 times the Cr(II) concentration, unless otherwise indicated.

Appendix 2.9. Derivation of equation 2.4 in Chapter 2



Charges are omitted for generality. The total concentration of chromium species is

$$[\text{Cr-R}]_{\text{tot}} = [(\text{H}_2\text{O})_5\text{Cr-R}] + [(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr-R}]$$

Substituting $K_f = [(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr-R}] / [(\text{H}_2\text{O})_5\text{Cr-R}][\text{SO}_4^{2-}]^{-1}$ into above equation and rearrangement yields

$$[(\text{H}_2\text{O})_5\text{Cr-R}] = \frac{[\text{Cr-R}]_{\text{tot}}}{1 + K_f[\text{SO}_4^{2-}]}$$

$$[(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr-R}] = \frac{K_f[\text{SO}_4^{2-}][\text{Cr-R}]_{\text{tot}}}{1 + K_f[\text{SO}_4^{2-}]}$$

The heterolysis rate is expressed by $-d[\text{Cr-R}]_{\text{tot}}/dt$, therefore

$$-d[\text{Cr-R}]_{\text{tot}}/dt = (k_0 + k_{\text{H}}[\text{H}^+])[(\text{H}_2\text{O})_5\text{Cr-R}] + (k_3[\text{H}^+] + k_4)[(\text{SO}_4)(\text{H}_2\text{O})_4\text{Cr-R}]$$

$$= (k_1[\text{H}^+] + k_0) \frac{[\text{Cr-R}]_{\text{tot}}}{1 + K_f[\text{SO}_4^{2-}]} + (k_3[\text{H}^+] + k_4) \frac{K_f[\text{SO}_4^{2-}][\text{Cr-R}]_{\text{tot}}}{1 + K_f[\text{SO}_4^{2-}]}$$

$$= \frac{k_1[\text{H}^+] + k_0 + (k_3[\text{H}^+] + k_4)K_f[\text{SO}_4^{2-}]}{1 + K_f[\text{SO}_4^{2-}]} [\text{Cr-R}]_{\text{tot}}$$

$$= k_{\text{obsd}}[\text{Cr-R}]_{\text{tot}}$$

and

$$k_{\text{obsd}} = \frac{k_1[\text{H}^+] + k_0 + (k_3[\text{H}^+] + k_4)K_f[\text{SO}_4^{2-}]}{1 + K_f[\text{SO}_4^{2-}]}$$

Substituting $K_a = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ into the total sulfate concentration, $[\text{SO}_4^{2-}]_t = [\text{SO}_4^{2-}] + [\text{HSO}_4^-]$ gives

$$[\text{SO}_4^{2-}] = \frac{K_a[\text{SO}_4^{2-}]_t}{K_a + [\text{H}^+]}$$

Substitution to above k_{obsd} yields

$$k_{\text{obsd}} = \frac{(k_1[\text{H}^+] + k_0) + (k_3K_fK_a[\text{H}^+] + k_4K_fK_a)\left(\frac{[\text{SO}_4^{2-}]_t}{K_a + [\text{H}^+]}\right)}{1 + \left(\frac{K_fK_a[\text{SO}_4^{2-}]_t}{K_a + [\text{H}^+]}\right)}$$

This is equation 2.4 in Chapter 2.

Appendix 3.1. Kinetic Results for the Homolysis of 4-Methylbenzylpentaqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 362 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
30.0	0.046	86.60	86.5	87.7
30.0	0.100	85.15	85.0	87.7
30.0	0.325	89.23	89.1	87.7
30.0	0.550	90.13	89.9	87.7
30.0	0.821	89.17	89.0	87.7
25.0	0.046	38.87	38.8	40.5
25.0	0.100	39.79	39.7	40.5
25.0	0.325	41.19	41.1	40.5
25.0	0.550	41.30	41.2	40.5
25.0	0.821	41.69	41.6	40.5
20.0	0.046	17.54	17.5	18.3
20.0	0.100	17.52	17.5	18.3
20.0	0.325	18.75	18.7	18.3
20.0	0.550	18.92	18.9	18.3
20.0	0.821	19.27	19.2	18.3

Appendix 3.2. Kinetic Results for the Homolysis of 4-Methylbenzylpentaqua-chromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 362 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
30.0	0.046	85.60	85.5	86.7
30.0	0.100	86.11	86.0	86.7
30.0	0.550	87.21	87.1	86.7
30.0	0.821	89.27	89.1	86.7
25.0	0.046	42.10	42.0	41.5
25.0	0.100	40.78	40.7	41.5
25.0	0.325	40.98	40.9	41.5
25.0	0.550	41.73	41.6	41.5
25.0	0.821	41.73	41.6	41.5
20.0	0.046	19.82	19.8	19.4
20.0	0.100	19.00	18.95	19.4
20.0	0.325	18.84	18.8	19.4
20.0	0.550	19.80	19.7	19.4
20.0	0.821	20.13	20.0	19.4

Appendix 3.3. Kinetic Results for the Homolysis of Benzylpentaquachromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 356 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homos}} \text{ s}^{-1}$	
			Obsd.	Calcd.
30.1	0.100	44.35	44.3	45.7
30.1	0.234	45.39	45.3	45.7
30.1	0.413	45.58	45.4	45.7
30.1	0.681	45.69	45.5	45.7
30.1	0.905	47.01	46.7	45.7
25.0	0.100	20.01	20.0	20.7
25.0	0.234	20.46	20.4	20.7
25.0	0.413	21.59	21.5	20.7
25.0	0.681	21.26	21.1	20.7
25.0	0.905	22.52	22.3	20.7
20.0	0.046	8.95	8.93	9.30
20.0	0.234	9.09	9.04	9.30
20.0	0.413	9.28	9.21	9.30
20.0	0.905	10.01	9.87	9.30

Appendix 3.4. Kinetic Results for the Homolysis of Benzylpentaquachromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 356 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
30.1	0.100	44.03	43.9	44.2
30.1	0.234	44.65	44.5	44.2
30.1	0.413	43.62	43.5	44.2
30.1	0.681	44.23	44.0	44.2
30.1	0.905	44.98	44.7	44.2
25.0	0.100	20.70	20.7	20.3
25.0	0.234	19.91	19.8	20.3
25.0	0.413	20.67	20.6	20.3
25.0	0.681	20.84	20.7	20.3
25.0	0.905	20.48	20.3	20.3
20.0	0.046	9.32	9.30	9.21
20.0	0.234	9.21	9.16	9.21
20.0	0.413	9.32	9.25	9.21
20.0	0.905	9.14	9.00	9.21

Appendix 3.5. Kinetic Results for the Homolysis of 4-Fluorobenzylpentaqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 354 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
32.2	0.034	54.40	54.3	57.4
32.2	0.150	55.09	55.0	57.4
32.2	0.431	57.74	57.6	57.4
32.2	0.712	61.23	61.1	57.4
32.2	0.948	62.30	62.2	57.4
25.0	0.100	17.58	17.5	18.7
25.0	0.239	18.11	18.1	18.7
25.0	0.431	18.55	18.5	18.7
25.0	0.712	19.06	19.0	18.7
25.0	0.948	19.65	19.6	18.7
18.0	0.239	5.76	5.74	5.95
18.0	0.431	5.95	5.93	5.95
18.0	0.712	6.10	6.08	5.95
18.0	0.948	6.31	6.28	5.95

Appendix 3.6. Kinetic Results for the Homolysis of 4-Fluorobenzylpenta-aqua-chromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 354 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
32.2	0.150	54.69	54.6	54.0
32.2	0.431	54.87	54.8	54.0
32.2	0.712	54.49	54.8	54.0
32.2	0.948	56.03	55.9	54.0
25.0	0.100	18.54	18.5	17.8
25.0	0.239	17.74	17.7	17.8
25.0	0.431	17.57	17.5	17.8
25.0	0.712	16.73	16.7	17.8
25.0	0.948	16.98	16.9	17.8
18.0	0.239	5.94	5.92	5.76
18.0	0.432	5.65	5.63	5.76
18.0	0.712	5.82	5.80	5.76
18.0	0.948	6.12	6.07	5.76

Appendix 3.7. Kinetic Results for the Homolysis of 2,4-Difluorobenzylpentaqua-chromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 350 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
34.9	0.046	2.401	2.40	2.47
34.9	0.100	2.428	2.42	2.47
34.9	0.325	2.483	2.47	2.47
34.9	0.550	2.512	2.50	2.47
34.9	0.821	2.523	2.51	2.47
30.0	0.046	1.061	1.06	1.13
30.0	0.100	1.150	1.15	1.13
30.0	0.325	1.154	1.15	1.13
30.0	0.550	1.178	1.17	1.13
30.0	0.821	1.226	1.22	1.13
25.0	0.046	0.4446	0.443	0.498
25.0	0.100	0.4884	0.486	0.498
25.0	0.325	0.5174	0.514	0.498
25.0	0.550	0.5296	0.525	0.498
25.0	0.821	0.5398	0.533	0.498

Appendix 3.8. Kinetic Results for the Homolysis of 2,4-Difluorobenzylpenta-aqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 350 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homol}}, \text{s}^{-1}$	
			Obsd.	Calcd.
34.9	0.046	2.445	2.44	2.47
34.9	0.100	2.428	2.48	2.47
34.9	0.325	2.477	2.47	2.47
34.9	0.550	2.489	2.48	2.47
34.9	0.821	2.483	2.47	2.47
30.0	0.046	1.133	1.13	1.15
30.0	0.100	1.130	1.13	1.15
30.0	0.325	1.161	1.16	1.15
30.0	0.550	1.185	1.18	1.15
30.0	0.821	1.184	1.17	1.15
25.0	0.046	0.5104	0.509	0.516
25.0	0.100	0.5113	0.509	0.516
25.0	0.325	0.5186	0.515	0.516
25.0	0.550	0.5186	0.514	0.516
25.0	0.821	0.5396	0.533	0.516

Appendix 3.9. Kinetic Results for the Homolysis of 3-Cyanobenzylpentaqua-chromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 350 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
35.0	0.150	1.238	1.24	1.28
35.0	0.431	1.260	1.26	1.28
35.0	0.712	1.295	1.29	1.28
35.0	0.948	1.375	1.37	1.28
25.0	0.150	0.2379	0.238	0.249
25.0	0.431	0.2418	0.241	0.249
25.0	0.712	0.2529	0.251	0.249
25.0	0.948	0.2577	0.255	0.249
19.4	0.150	0.0912	0.0910	0.0950
19.4	0.431	0.0946	0.0939	0.0950
19.4	0.712	0.0992	0.0981	0.0950
19.4	0.948	0.1041	0.1010	0.0950

Appendix 3.10. Kinetic Results for the Homolysis of 3-Cyanobenzylpenta-aqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 350 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
35.0	0.150	1.109	1.11	1.19
35.0	0.431	1.171	1.17	1.19
35.0	0.712	1.256	1.25	1.19
35.0	0.948	1.298	1.29	1.19
25.0	0.043	0.2063	0.206	0.223
25.0	0.150	0.2151	0.215	0.223
25.0	0.431	0.2267	0.226	0.223
25.0	0.712	0.2323	0.231	0.223
25.0	0.948	0.2439	0.242	0.223
19.4	0.150	0.0813	0.0811	0.0830
19.4	0.431	0.0839	0.0832	0.0830
19.4	0.712	0.0843	0.0832	0.0830
19.4	0.948	0.0874	0.0859	0.0830

Appendix 3.11. Kinetic Results for the Homolysis of 3,5-Difluorobenzylpentaqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 348 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
36.5	0.042	1.675	1.67	1.78
36.5	0.100	1.677	1.67	1.78
36.5	0.337	1.744	1.73	1.78
36.6	0.574	1.794	1.78	1.78
36.6	0.717	1.879	1.86	1.78
36.6	0.860	1.899	1.88	1.78
31.0	0.042	0.7318	0.729	0.739
31.0	0.100	0.7419	0.738	0.739
31.0	0.337	0.7600	0.754	0.739
31.0	0.574	0.7813	0.772	0.739
31.0	0.717	0.7874	0.777	0.739
31.0	0.860	0.7827	0.770	0.739
25.0	0.042	0.2690	0.267	0.278
25.0	0.100	0.2682	0.266	0.278
25.0	0.337	0.2788	0.275	0.278
25.0	0.574	0.2847	0.279	0.278
25.0	0.717	0.2895	0.283	0.278
25.0	0.860	0.2927	0.285	0.278

Appendix 3.12. Kinetic Results for the Homolysis of 2-Cyanobenzylpentaqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ Observed at 316 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homo}}, \text{s}^{-1}$	
			Obsd.	Calcd.
34.4	0.022	15.86	15.4	16.0
34.4	0.100	16.02	15.5	16.0
34.4	0.346	16.66	16.1	16.0
34.4	0.581	16.73	16.2	16.0
34.4	0.870	17.40	16.9	16.0
23.9	0.022	2.891	2.76	2.87
23.9	0.100	2.941	2.81	2.87
23.9	0.346	3.017	2.88	2.87
23.9	0.581	3.086	2.95	2.87
23.9	0.870	3.209	3.07	2.87
17.0	0.100	0.873	0.822	0.870
17.0	0.346	0.919	0.867	0.870
17.0	0.581	0.924	0.871	0.870
17.0	0.870	0.970	0.916	0.870

Appendix 3.13. Kinetic Results for the Homolysis of 2-Cyanobenzylpentaqua-chromium(III) with Scavenger Aqueous $\text{Fe}(\text{ClO}_4)_3$ Observed at 316 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homO}}, \text{s}^{-1}$	
			Obsd.	Calcd.
34.4	0.100	1.880	1.83	1.76
34.4	0.346	1.779	1.73	1.76
34.4	0.581	1.788	1.74	1.76
34.4	0.870	1.861	1.81	1.76
23.9	0.100	0.3084	0.295	0.313
23.9	0.346	0.3127	0.299	0.313
23.9	0.581	0.3224	0.309	0.313
23.9	0.870	0.3311	0.317	0.313
17.0	0.100	0.0908	0.0857	0.0941
17.0	0.346	0.1014	0.0962	0.0941
17.0	0.581	0.1045	0.0982	0.0941
17.0	0.870	0.1132	0.1078	0.0941

Appendix 3.14. Kinetic Results for the Homolysis of 2-Cyanobenzylpenta-aqua-chromium(III) with Scavenger $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ Observed at 316 nm in 1.00 M $\text{HClO}_4/\text{NaClO}_4$

Temp °C	$[\text{H}^+]$ M	$10^4 \times k_{\text{obsd}}$ s^{-1}	$10^4 \times k_{\text{homol}}, \text{s}^{-1}$	
			Obsd.	Calcd.
34.4	0.022	16.94	16.5	17.0
34.4	0.100	17.13	16.6	17.0
34.4	0.346	17.51	17.0	17.0
34.4	0.581	17.44	16.9	17.0
34.4	0.870	18.31	17.8	17.0
23.9	0.022	3.149	3.02	3.07
23.9	0.100	3.155	3.03	3.07
23.9	0.346	3.237	3.10	3.07
23.9	0.581	3.253	3.12	3.07
23.9	0.870	3.401	3.26	3.07
17.0	0.100	0.935	0.884	0.930
17.0	0.346	0.958	0.906	0.930
17.0	0.581	0.995	0.942	0.930
17.0	0.870	1.021	0.967	0.930

Appendix 3.15. Kinetic Results for the Homolysis of 4-Cyanobenzylpentaqua-chromium(III) Observed at 310 nm in 1.00 M HClO₄/NaClO₄

Temp °C	[H ⁺] M	10 ⁴ × <i>k</i> _{obsd} s ⁻¹	10 ⁴ × <i>k</i> _{homo} , s ⁻¹	
			Obsd.	Calcd. ^c
31.0 ^a	0.0230	13.30	10.68	11.16
31.0 ^a	0.0424	13.54	10.32	10.79
31.0 ^a	0.0610	13.52	9.94	10.57
31.0 ^a	0.100	12.92	8.90	10.30
31.0 ^a	0.241	14.02	9.44	9.96
31.0 ^a	0.430	13.97	9.17	9.82
31.0 ^a	0.714	14.37	9.44	9.74
31.0 ^a	0.951	15.30	10.32	9.71
31.0 ^b	0.0230	14.59	11.97	11.16
31.0 ^b	0.0424	14.44	11.22	10.79
31.0 ^b	0.0610	14.60	11.02	10.57
31.0 ^b	0.100	14.36	10.34	10.30
31.0 ^b	0.241	14.41	9.83	9.96
31.0 ^b	0.430	14.76	9.96	9.82
31.0 ^b	0.714	15.03	10.10	9.74
31.0 ^b	0.951	15.50	10.52	9.71
36.6 ^a	0.0230	33.95	28.98	28.52
36.6 ^a	0.0424	33.00	26.66	27.55
36.6 ^a	0.0610	36.30	29.12	26.95
36.6 ^a	0.100	33.87	25.61	26.19
36.6 ^a	0.241	35.40	25.69	25.17

36.6 ^a	0.430	33.00	22.69	24.74
36.6 ^a	0.714	34.83	24.18	24.50
36.6 ^a	0.951	36.16	25.38	24.41
36.6 ^b	0.0230	33.09	28.12	28.52
36.6 ^b	0.0424	31.94	25.60	27.55
36.6 ^b	0.0610	33.49	26.31	26.95
36.6 ^b	0.100	32.73	24.47	26.19
36.6 ^b	0.241	33.86	24.15	25.17
36.6 ^b	0.430	34.29	23.98	24.74
36.6 ^b	0.714	36.17	25.52	24.50
36.6 ^b	0.951	35.97	25.19	24.41

^a With scavenger $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$. ^b With scavenger $\text{Fe}(\text{ClO}_4)_3$. ^c Calculated from the rate law and activation parameters given in the text.

Appendix 3.16. Stoichiometry Results for Homolysis of Substituted Benzylpenta-aquachromium(III) Complexes in 0.10 M HClO₄ at Ambient Temperature

Substituent	Oxidant	Oxidant per Cr Initial	Oxidant Consumed per Cr
4-Methyl	Co(NH ₃) ₅ Cl ²⁺	5 : 1	1.00 : 1
		14 : 1	1.02 : 1
	Co(NH ₃) ₅ Br ²⁺	5 : 1	1.96 : 1
		7 : 1	1.96 : 1
		10 : 1	2.03 : 1
	Fe(OH ₂) ₆ ³⁺	4 : 1	1.97 : 1
		8 : 1	2.03 : 1
		12 : 1	2.01 : 1
4-H	Co(NH ₃) ₅ Cl ²⁺	5 : 1	0.98 : 1
		14 : 1	1.03 : 1
	Co(NH ₃) ₅ Br ²⁺	3 : 1	1.95 : 1
		5 : 1	1.95 : 1
		8 : 1	1.98 : 1
	Fe(OH ₂) ₆ ³⁺	3 : 1	1.72 : 1
		6 : 1	1.90 : 1
		9 : 1	2.02 : 1
4-Fluoro	Co(NH ₃) ₅ Cl ²⁺	5 : 1	0.98 : 1
		14 : 1	1.02 : 1
	Co(NH ₃) ₅ Br ²⁺	5 : 1	1.98 : 1
		7 : 1	1.97 : 1
		10 : 1	1.98 : 1

Appendix 3.16. continued

	$\text{Fe}(\text{OH}_2)_6^{3+}$	4 : 1	1.97 : 1
		8 : 1	2.00 : 1
		12 : 1	2.00 : 1
2,4-Difluoro	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	5 : 1	0.98 : 1
		14 : 1	1.02 : 1
	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	5 : 1	1.96 : 1
		7 : 1	1.95 : 1
		10 : 1	1.98 : 1
	$\text{Fe}(\text{OH}_2)_6^{3+}$	3 : 1	1.50 : 1
		6 : 1	1.68 : 1
		9 : 1	1.80 : 1
3,5-Difluoro	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	5 : 1	1.01 : 1
		14 : 1	1.03 : 1
	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	5 : 1	1.96 : 1
		7 : 1	1.95 : 1
		10 : 1	1.95 : 1
	$\text{Fe}(\text{OH}_2)_6^{3+}$	4 : 1	0.98 : 1
		8 : 1	1.03 : 1
		13 : 1	1.03 : 1
2-Cyano	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	5 : 1	1.01 : 1
		14 : 1	1.03 : 1
	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	5 : 1	1.94 : 1
		7 : 1	1.95 : 1
		10 : 1	1.95 : 1
	$\text{Fe}(\text{OH}_2)_6^{3+}$	4 : 1	1.04 : 1

Appendix 3.16. continued

		8 : 1	1.05 : 1
		13 : 1	1.07 : 1
3-Cyano	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	5 : 1	1.00 : 1
		14 : 1	1.01 : 1
	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	4 : 1	1.90 : 1
		6 : 1	1.90 : 1
		8 : 1	1.94 : 1
	$\text{Fe}(\text{OH}_2)_6^{3+}$	4 : 1	1.02 : 1
		8 : 1	1.00 : 1
		13 : 1	1.02 : 1
4-Cyano	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	7 : 1	0.69 : 1
		14 : 1	0.76 : 1
	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	6 : 1	1.64 : 1
		7 : 1	1.65 : 1
		10 : 1	1.75 : 1
	$\text{Fe}(\text{OH}_2)_6^{3+}$	5 : 1	0.74 : 1
		10 : 1	0.87 : 1
		15 : 1	0.88 : 1

Appendix 4.1. Kinetic Results for the Heterolysis of Benzylpentaquachromium(III)
in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc], M	pH	$10^3 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^3 \times k_{\text{calcs}}, \text{ s}^{-1}$
0.040	4.73	0.259	0.236
0.100	4.73	0.676	0.721
0.200	4.73	1.40	1.57
0.400	3.01	2.35	2.19
0.400	4.73	3.22	3.31
0.600	3.01	4.24	4.25
0.600	4.04	7.68	7.66
0.600	4.36	7.08	6.87
0.600	4.73	5.08	5.06
0.600	5.02	3.73	3.50
0.800	3.01	6.71	6.58
0.800	4.73	7.89	6.81
1.000	3.01	8.97	9.12
1.000	4.73	9.56	8.56

Appendix 4.2. Kinetic Results for the Heterolysis of 2-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] ₀ , M	pH	$10^4 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^4 \times k_{\text{calc}}, \text{ s}^{-1}$
0.100	4.73	1.20	1.14
0.200	4.73	1.51	1.53
0.400	4.73	2.17	2.25
0.401	2.96	1.70	1.77
0.401	3.07	1.98	1.99
0.600	2.96	2.89	2.88
0.600	3.55	3.92	4.02
0.600	3.99	3.95	4.11
0.600	3.99	4.12	4.11
0.600	4.20	3.97	3.93
0.600	4.34	3.91	3.73
0.600	4.35	3.52	3.71
0.600	4.73	2.81	2.95
0.600	4.73	3.10	2.95
0.800	3.10	4.49	4.48
0.800	4.73	3.78	3.64
0.802	2.95	4.13	4.06
0.802	2.96	3.91	4.09
1.000	2.90	5.44	5.10
1.000	2.96	5.47	5.31
1.000	3.09	5.93	5.74

Appendix 4.3. Kinetic Results for the Heterolysis of 3-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] _i , M	pH	$10^3 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{ s}^{-1}$
0.040	4.73	0.115	0.114
0.200	4.73	0.595	0.621
0.400	2.96	1.12	1.07
0.400	3.13	1.30	1.30
0.400	4.73	1.21	1.26
0.600	3.13	2.25	2.31
0.600	3.33	2.53	2.66
0.600	3.55	2.91	2.91
0.600	3.71	3.01	3.01
0.600	4.01	2.98	2.97
0.600	4.33	2.70	2.64
0.600	4.73	1.83	1.90
0.600	4.99	1.45	1.37
0.800	3.13	3.33	3.41
0.800	4.73	2.60	2.54
0.802	2.96	3.01	3.00
1.000	2.96	4.09	4.06
1.000	3.13	4.63	4.55
1.000	4.73	3.36	3.18

Appendix 4.4. Kinetic Results for the Heterolysis of 4-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] _i , M	pH	$10^3 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{ s}^{-1}$
0.100	4.73	0.223	0.217
0.200	4.73	0.390	0.401
0.400	3.11	0.820	0.848
0.400	4.73	0.754	0.772
0.600	3.11	1.49	1.45
0.600	3.55	1.75	1.79
0.600	4.00	1.78	1.79
0.600	4.33	1.57	1.58
0.600	4.73	1.14	1.14
0.800	3.11	2.12	2.10
0.800	4.73	1.54	1.52
1.000	3.11	2.87	2.77
1.000	4.73	1.91	1.89

Appendix 4.5. Kinetic Results for the Homolysis of Benzylpentaquachromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] _i , M	pH	$10^3 \times k_{\text{het}}, \text{ s}^{-1}$	$10^3 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{ s}^{-1}$
0.040	4.73	0.2362	3.17	3.115
0.100	4.73	0.721	3.82	3.896
0.200	4.73	1.576	4.74	4.901
0.400	4.73	3.314	6.59	6.731
0.600	3.01	4.252	6.52	6.912
0.600	4.04	7.660	11.10	10.99
0.600	4.73	5.060	8.70	8.510
0.600	5.02	3.496	7.32	6.963
0.800	4.73	6.808	11.35	10.28
1.000	4.73	8.557	13.41	12.04

Appendix 4.6. Kinetic Results for the Homolysis of 2-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] _i , M	pH	$10^3 \times k_{\text{het}}, \text{s}^{-1}$	$10^3 \times k_{\text{obsd}}, \text{s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{s}^{-1}$
0.100	4.73	0.1142	0.4302	0.4268
0.200	4.73	0.1534	0.4564	0.4610
0.400	4.73	0.2248	0.5242	0.5297
0.600	3.99	0.4112	0.7088	0.7193
0.600	4.20	0.3925	0.7073	0.6987
0.600	4.35	0.3709	0.6508	0.6762
0.600	4.73	0.2945	0.5885	0.5984
0.800	3.10	0.4476	0.7773	0.7729
0.800	4.73	0.3638	0.6782	0.6672
0.802	2.95	0.4054	0.7462	0.7365
1.000	2.90	0.5096	0.8880	0.8388
1.000	3.09	0.5733	0.9330	0.8954

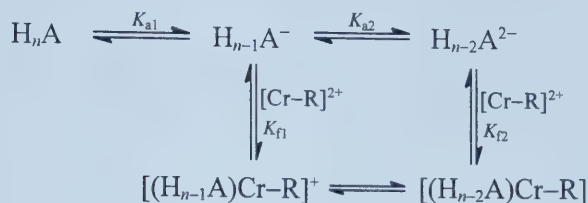
Appendix 4.7. Kinetic Results for the Homolysis of 3-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc], M	pH	$10^3 \times k_{\text{het}}, \text{s}^{-1}$	$10^3 \times k_{\text{obsd}}, \text{s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{s}^{-1}$
0.040	4.73	0.1143	0.5556	0.5566
0.200	4.73	0.6206	1.138	1.142
0.400	4.73	1.259	1.756	1.794
0.600	3.13	2.312	2.681	2.731
0.600	3.33	2.655	2.966	3.107
0.600	3.55	2.908	3.389	3.391
0.600	3.71	3.003	3.518	3.503
0.600	4.01	2.970	3.510	3.491
0.600	4.33	2.637	3.239	3.170
0.600	4.73	1.897	2.361	2.438
0.600	4.99	1.366	1.993	1.909
0.800	3.13	3.405	3.758	3.846
0.800	4.73	2.536	3.164	3.079
0.802	2.96	2.996	3.399	3.407
1.000	3.13	4.543	5.086	5.000
1.000	4.73	3.175	3.885	3.720

Appendix 4.8. Kinetic Results for the Homolysis of 4-Cyanobenzylpentaqua-chromium(III) in Acetate/Acetic Acid Buffers at 25 °C in 1.00 M NaOAc/NaClO₄

[OAc] _t , M	pH	$10^3 \times k_{\text{het}}, \text{ s}^{-1}$	$10^3 \times k_{\text{obsd}}, \text{ s}^{-1}$	$10^3 \times k_{\text{calc}}, \text{ s}^{-1}$
0.400	3.11	0.8483	1.255	1.286
0.600	3.11	1.455	1.963	1.910
0.600	3.55	1.786	2.233	2.274
0.600	4.00	1.790	2.280	2.295
0.600	4.33	1.583	2.088	2.094
0.600	4.73	1.144	1.668	1.659
0.800	3.11	2.104	2.584	2.570
0.800	4.73	1.516	2.065	2.032
1.000	4.73	1.888	2.407	2.405

Appendix 5.1. Derivation of equation 5.3 to 5.5 in Chapter 5.



The equilibrium expression is

$$K_{f1} = \frac{[(\text{H}_{n-1}\text{A})\text{Cr-R}]}{[\text{Cr-R}][\text{H}_{n-1}\text{A}]} \quad (\text{A.1})$$

$$K_{f2} = \frac{[(\text{H}_{n-2}\text{A})\text{Cr-R}]}{[\text{Cr-R}][\text{H}_{n-2}\text{A}]} \quad (\text{A.2})$$

Charges are omitted for generality. The total concentration of chromium species is

$$[\text{Cr-R}]_{\text{tot}} = [\text{Cr-R}] + [(\text{H}_{n-1}\text{A})\text{Cr-R}] + [(\text{H}_{n-2}\text{A})\text{Cr-R}] \quad (\text{A.3})$$

Substituting eq A.1 and A.2 into eq A.3 and rearrangement yields eq A.4.

$$[\text{Cr-R}] = \frac{[\text{Cr-R}]_{\text{tot}}}{1 + K_{f1}[\text{H}_{n-1}\text{A}] + K_{f2}[\text{H}_{n-2}\text{A}]} \quad (\text{A.4})$$

Substituting eq A.4 into eq A.1 and A.2, and rearrangement gives

$$[(H_{n-1}A)Cr-R] = \frac{K_{f1} [H_{n-1}A][Cr-R]_{tot}}{1 + K_{f1} [H_{n-1}A] + K_{f2}[H_{n-2}A]}$$

$$[(H_{n-2}A)Cr-R] = \frac{K_{f2} [H_{n-2}A][Cr-R]_{tot}}{1 + K_{f1} [H_{n-1}A] + K_{f2}[H_{n-2}A]}$$

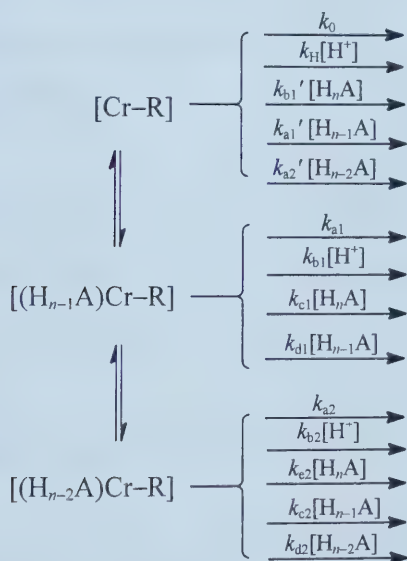
Definining $F_m = 1 + K_{f1}[H_{n-1}A] + K_{f2}[H_{n-2}A]$ and substituting to above equations yields

$$[Cr-R] = (F_m)^{-1}[Cr-R]_{tot} \quad (A.5)$$

$$[(H_{n-1}A)Cr-R] = (F_m)^{-1}K_{f1}[H_{n-1}A][Cr-R]_{tot} \quad (A.6)$$

$$[(H_{n-2}A)Cr-R] = (F_m)^{-1}K_{f2}[H_{n-2}A][Cr-R]_{tot} \quad (A.7)$$

The reaction pathways of heterolysis are shown in the following scheme.



The heterolysis rate is expressed by $-d[Cr-R]_{tot}/dt$, therefore

$$-d[Cr-R]_{tot}/dt = (k_0 + k_{H1}[H^+] + k_{b1}'[H_nA] + k_{a1}'[H_{n-1}A] + k_{a2}'[H_{n-2}A])[Cr-R]$$

$$\begin{aligned}
& + (k_{a1} + k_{b1}[H^+] + k_{c1}[H_nA] + k_{d1}[H_{n-1}A])(H_{n-1}A)Cr-R \\
& + (k_{a2} + k_{b2}[H^+] + k_{c2}[H_nA] + k_{c2}[H_{n-1}A] + k_{d2}[H_{n-2}A])(H_{n-2}A)Cr-R \\
& \qquad \qquad \qquad (A.8)
\end{aligned}$$

Substituting eq A.5–A.7 into eq A.8 gives

$$\begin{aligned}
-d[Cr-R]_{\text{tot}}/dt &= (k_0 + k_H[H^+] + k_{a1}'[H_{n-1}A] + k_{b1}'[H_nA] + k_{a2}'[H_{n-2}A])(F_m)^{-1}[Cr-R]_{\text{tot}} \\
& + (k_{a1} + k_{b1}[H^+] + k_{c1}[H_nA] + k_{d1}[H_{n-1}A])(F_m)^{-1}K_{f1}[H_{n-1}A][Cr-R]_{\text{tot}} \\
& + (k_{a2} + k_{b2}[H^+] + k_{c2}[H_{n-1}A] + k_{d2}[H_{n-2}A])(F_m)^{-1}K_{f2}[H_{n-2}A][Cr-R]_{\text{tot}} \\
& = \{(k_0 + k_H[H^+] + k_{a1}'[H_{n-1}A] + k_{b1}'[H_nA] + k_{a2}'[H_{n-2}A]) \\
& + (k_{a1} + k_{b1}[H^+] + k_{c1}[H_nA] + k_{d1}[H_{n-1}A])K_{f1}[H_{n-1}A] \\
& + (k_{a2} + k_{b2}[H^+] + k_{c2}[H_{n-1}A] + k_{c2}[H_{n-1}A] \\
& + k_{d2}[H_{n-2}A])K_{f2}[H_{n-2}A]\}(F_m)^{-1}[Cr-R]_{\text{tot}} \\
& = k_{\text{obsd}}[Cr-R]_{\text{tot}}
\end{aligned}$$

$$\begin{aligned}
\text{Thus } k_{\text{obsd}} &= \{(k_0 + k_H[H^+] + k_{a1}'[H_{n-1}A] + k_{b1}'[H_nA] + k_{a2}'[H_{n-2}A]) \\
& + (k_{a1} + k_{b1}[H^+] + k_{c1}[H_nA] + k_{d1}[H_{n-1}A])K_{f1}[H_{n-1}A] \\
& + (k_{a2} + k_{b2}[H^+] + k_{c2}[H_{n-1}A] + k_{c2}[H_{n-1}A] + k_{d2}[H_{n-2}A])K_{f2}[H_{n-2}A]\}(F_m)^{-1}
\end{aligned}$$

This can be rearranged to equation 5.3 in Chapter 5.

$$\begin{aligned}
k_{\text{obsd}} &= (F_m)^{-1}(k_0 + k_H[H^+] + k_{a1}K_{f1}[H_{n-1}A] + k_{a1}'[H_{n-1}A] + k_{b1}K_{f1}[H^+][H_{n-1}A] + k_{b1}'[H_nA] \\
& + k_{a2}K_{f2}[H_{n-2}A] + k_{a2}'[H_{n-2}A] + k_{b2}K_{f2}[H^+][H_{n-2}A] + k_{c1}K_{f1}[H_{n-1}A][H_nA] \\
& + k_{c2}K_{f2}[H_{n-2}A][H_nA] + k_{c2}K_{f2}[H_{n-2}A][H_{n-1}A] + k_{d1}K_{f1}[H_{n-1}A]^2 + k_{d2}K_{f2}[H_{n-2}A]^2) \\
& \qquad \qquad \qquad (5.3)
\end{aligned}$$

For a tribasic acid,



The total concentration of the various conjugate base species is

$$[\text{A}]_{\text{tot}} = [\text{H}_3\text{A}] + [\text{H}_2\text{A}] + [\text{HA}] + [\text{A}] \quad (\text{A.9})$$

The acid dissociation constants are given by

$$K_{a1} = [\text{H}_2\text{A}][\text{H}^+]/[\text{H}_3\text{A}]$$

$$K_{a2} = [\text{HA}][\text{H}^+]/[\text{H}_2\text{A}]$$

$$K_{a3} = [\text{A}][\text{H}^+]/[\text{HA}]$$

Substituting into eq A.9 and rearrangement yields

$$[\text{H}_3\text{A}] = \frac{[\text{H}^+]^3 [\text{A}]_{\text{tot}}}{[\text{H}^+]^3 + K_{a1} [\text{H}^+]^2 + K_{a1} K_{a2} [\text{H}^+] + K_{a1} K_{a2} K_{a3}} \quad (\text{A.10})$$

$$[\text{H}_2\text{A}] = \frac{K_{a1} [\text{H}^+]^2 [\text{A}]_{\text{tot}}}{[\text{H}^+]^3 + K_{a1} [\text{H}^+]^2 + K_{a1} K_{a2} [\text{H}^+] + K_{a1} K_{a2} K_{a3}} \quad (\text{A.11})$$

$$[\text{HA}] = \frac{K_{a1} K_{a2} [\text{H}^+] [\text{A}]_{\text{tot}}}{[\text{H}^+]^3 + K_{a1} [\text{H}^+]^2 + K_{a1} K_{a2} [\text{H}^+] + K_{a1} K_{a2} K_{a3}} \quad (\text{A.12})$$

$$[\text{A}] = \frac{K_{a1} K_{a2} K_{a3} [\text{A}]_{\text{tot}}}{[\text{H}^+]^3 + K_{a1} [\text{H}^+]^2 + K_{a1} K_{a2} [\text{H}^+] + K_{a1} K_{a2} K_{a3}} \quad (\text{A.13})$$

Defining $F_A = [A]_{\text{tot}}([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})^{-1}$, and substituting into eq A.10–A.13, one can obtain

$$[H_3A] = [H^+]^3 F_A \quad (\text{A.14})$$

$$[H_2A] = K_{a1}[H^+]^2 F_A \quad (\text{A.15})$$

$$[HA] = K_{a1}K_{a2}[H^+] F_A \quad (\text{A.16})$$

$$[A] = K_{a1}K_{a2}K_{a3} F_A \quad (\text{A.17})$$

Substituting eq A.14–A.17 into eq 5.3 in Chapter 5 yields

$$\begin{aligned} k_{\text{obsd}} &= (F_m)^{-1}(k_0 + k_H[H^+] + k_{a1}K_{f1}K_{a1}[H^+]^2 F_A + k_{a1}'K_{a1}[H^+]^2 F_A + k_{b1}K_{f1}K_{a1}[H^+]^3 F_A \\ &\quad + k_{b1}'[H^+]^3 F_A + k_{a2}K_{f2}K_{a1}K_{a2}[H^+] F_A + k_{a2}'K_{a1}K_{a2}[H^+] F_A + k_{b2}K_{f2}K_{a1}K_{a2}[H^+]^2 F_A \\ &\quad + k_{c1}K_{f1}K_{a1}[H^+]^5 F_A^2 + k_{e2}K_{f2}K_{a1}K_{a2}[H^+]^4 F_A^2 + k_{c2}K_{f2}K_{a1}^2 K_{a2}[H^+]^3 F_A^2 \\ &\quad + k_{d1}K_{f1}K_{a1}^2 [H^+]^4 F_A^2 + k_{d2}K_{f2}K_{a1}^2 K_{a2}^2 [H^+]^2 F_A^2) \\ &= (F_m)^{-1}(k_0 + k_H[H^+] + F_A \{ (k_{a2}K_{f2}K_{a1}K_{a2} + k_{a2}'K_{a1}K_{a2})[H^+] + K_{a1}(k_{a1}K_{f1} + k_{a1}' \\ &\quad + k_{b2}K_{f2}K_{a2})[H^+]^2 + (k_{b1}K_{f1}K_{a1} + k_{b1}')[H^+]^3 + F_A(k_{d2}K_{f2}K_{a1}^2 K_{a2}^2 [H^+]^2 \\ &\quad + k_{c2}K_{f2}K_{a1}^2 K_{a2}[H^+]^3 + k_{e2}K_{f2}K_{a1}K_{a2}[H^+]^4 + k_{d1}K_{f1}K_{a1}^2 [H^+]^4 + k_{c1}K_{f1}K_{a1}[H^+]^5) \}) \end{aligned} \quad (\text{A.18})$$

Definining $k_1 = k_{a2}K_{f2} + k_{a2}'$, $k_2 = k_{a1}K_{f1} + k_{a1}' + k_{b2}K_{f2}K_{a2}$, $k_3 = k_{b1}K_{f1}K_{a1} + k_{b1}'$, $k_4 = k_{d2}K_{f2}$, $k_5 = k_{c2}K_{f2}$, $k_6 = k_{d1}K_{f1}K_{a1} + k_{e2}K_{f2}K_{a2}$, $k_7 = k_{c1}K_{f1}$ and substituting into eq A.18 gives equation 5.4 in Chapter 5.

$$\begin{aligned} k_{\text{obsd}} &= (F_m)^{-1}(k_0 + k_H[H^+] + F_A \{ k_1 K_{a1} K_{a2} [H^+] + k_2 K_{a1} [H^+]^2 + k_3 [H^+]^3 \\ &\quad + F_A (k_4 (K_{a1} K_{a2})^2 [H^+]^2 + k_5 K_{a1}^2 K_{a2} [H^+]^3 + k_6 K_{a1} [H^+]^4 + k_7 K_{a1} [H^+]^5) \}) \end{aligned} \quad (\text{5.4})$$

For acetic acid, all terms containing k_{a2} , k_{b2} , k_{c2} , k_{d2} and K_{a2} , K_{f2} are zero, and $F_m = 1 + K_{f1}[\text{OAc}^-]$, $F_A = [\text{OAc}]_{\text{tot}}[\text{H}^+]^{-2}(K_{a1} + [\text{H}^+])^{-1}$. Then eq 5.4 simplifies to

$$\begin{aligned}
 k_{\text{obsd}} &= (F_m)^{-1}(k_0 + k_{\text{H}}[\text{H}^+] + \{k_2K_{a1}[\text{H}^+]^2 + k_3[\text{H}^+]^3 + (k_6K_{a1}^2[\text{H}^+]^4 + k_7K_{a1}[\text{H}^+]^5)F_A\}F_A) \\
 &= (1 + K_{f1}[\text{OAc}^-])^{-1}(k_0 + k_{\text{H}}[\text{H}^+] + \{k_2K_{a1}[\text{H}^+]^2 + k_3[\text{H}^+]^3 + (k_6K_{a1}^2[\text{H}^+]^4 + \\
 &\quad k_7K_{a1}[\text{H}^+]^5)([\text{OAc}]_{\text{tot}}[\text{H}^+]^{-2}(K_{a1} + [\text{H}^+])^{-1})\}([\text{OAc}]_{\text{tot}}[\text{H}^+]^{-2}(K_{a1} + [\text{H}^+])^{-1}) \\
 &= (1 + K_{f1}[\text{OAc}^-])^{-1}(k_0 + k_{\text{H}}[\text{H}^+] + \{k_2K_{a1} + k_3[\text{H}^+] + (k_6K_{a1}^2 + \\
 &\quad k_7K_{a1}[\text{H}^+])([\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1})\}([\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1})
 \end{aligned} \tag{A.19}$$

Since $[\text{OAc}^-] = K_{a1}[\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1}$, substituting into eq A.19 yields eq 5.5 in Chapter 5.

$$\begin{aligned}
 k_{\text{obsd}} &= (1 + K_{f1}K_{a1}(K_{a1} + [\text{H}^+])^{-1}[\text{OAc}]_{\text{tot}})^{-1}(k_0 + k_{\text{H}}[\text{H}^+] + \{k_2K_{a1} + k_3[\text{H}^+] + (k_6K_{a1}^2 + \\
 &\quad k_7K_{a1}[\text{H}^+])([\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1})\}([\text{OAc}]_{\text{tot}}(K_{a1} + [\text{H}^+])^{-1})
 \end{aligned} \tag{5.5}$$

Appendix 5.2. Kinetic Results for the Heterolysis of Benzylpentaquachromium(III) in NaH_2PO_4 - Na_2HPO_4 Buffers at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$

$[\text{PO}_4]_t$, M	pH	$10^2 \times k_{\text{obsd}}$, s^{-1}	$10^2 \times k_{\text{calc}}$, s^{-1}
0.050	3.25	0.717	0.715
0.100	3.65	1.63	1.64
0.100	3.65	1.69	1.64
0.200	2.10	0.400	0.439
0.200	3.74	2.95	3.24
0.200	3.74	3.22	3.24
0.300	2.08	0.661	0.620
0.300	2.37	0.900	0.868
0.300	2.73	1.20	1.25
0.300	3.01	1.65	1.67
0.300	3.01	1.74	1.67
0.300	3.25	2.26	2.22
0.300	3.25	2.27	2.22
0.300	3.51	3.28	3.11
0.300	3.65	3.89	3.75
0.300	3.82	5.01	4.69
0.300	3.94	5.46	5.45
0.300	3.94	5.61	5.45
0.300	4.14	7.14	6.84
0.300	4.14	7.43	6.84
0.300	4.28	8.34	7.84
0.400	2.10	0.821	0.820

0.400	3.82	5.09	5.49
0.400	3.82	5.37	5.49
0.500	2.10	0.949	0.992
0.500	3.90	6.07	6.64
0.600	2.08	1.16	1.13
0.600	3.85	6.24	6.81
0.600	3.85	6.75	6.81
0.700	3.85	7.50	7.21
0.900	2.11	1.69	1.60

Appendix 5.3. Kinetic Results for the Heterolysis of 2-Cyanobenzylpentaqua-chromium(III) in NaH_2PO_4 - Na_2HPO_4 Buffers at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$

$[\text{PO}_4]_{\text{t}}, \text{M}$	pH	$10^2 \times k_{\text{obsd}}, \text{s}^{-1}$	$10^2 \times k_{\text{calc}}, \text{s}^{-1}$
0.05	2.09	0.0219	0.0225
0.050	4.23	0.328	0.346
0.100	2.08	0.0458	0.0432
0.200	2.10	0.0823	0.0846
0.200	4.13	0.906	0.887
0.300	2.08	0.124	0.119
0.300	4.14	1.25	1.18
0.400	2.13	0.161	0.161
0.400	4.17	1.47	1.45
0.500	1.49	0.0804	0.0789
0.500	2.12	0.194	0.191
0.500	2.65	0.285	0.300
0.500	3.17	0.480	0.459
0.500	3.71	0.936	0.861
0.500	3.95	1.32	1.20
0.500	3.97	1.27	1.23
0.500	4.10	1.31	1.47
0.500	4.13	1.38	1.534
0.500	4.43	2.37	2.22
0.500	4.68	3.07	2.84
0.500	4.86	3.12	3.25
0.500	4.86	3.45	3.25

0.600	2.08	0.219	0.211
0.600	4.15	1.57	1.71
0.700	2.09	0.244	0.240
0.700	4.18	1.92	1.89
0.900	2.15	0.318	0.305
0.900	4.18	1.93	2.07

Appendix 5.4. Kinetic Results for the Heterolysis of 3-Cyanobenzylpenta-aqua-chromium(III) in NaH_2PO_4 - Na_2HPO_4 Buffers at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$

$[\text{PO}_4]_t$, M	pH	$10^2 \times k_{\text{obsd}}$, s^{-1}	$10^2 \times k_{\text{calc}}$, s^{-1}
0.100	2.10	0.122	0.131
0.200	2.10	0.265	0.257
0.200	3.92	2.80	2.96
0.200	3.92	3.02	2.96
0.300	2.12	0.414	0.388
0.300	2.40	0.542	0.553
0.300	2.44	0.574	0.580
0.300	2.84	0.923	0.923
0.300	3.00	1.09	1.12
0.300	3.00	1.13	1.12
0.300	3.31	1.62	1.69
0.300	3.57	2.43	2.41
0.300	3.57	2.55	2.41
0.300	3.75	2.92	3.05
0.300	3.77	2.93	3.13
0.300	3.87	3.52	3.54
0.300	3.98	3.97	4.01
0.300	3.98	3.97	4.01
0.300	3.98	4.18	4.01
0.300	3.98	4.18	4.01
0.300	4.24	4.76	5.14
0.300	4.24	4.78	5.14

0.300	4.53	6.07	6.25
0.400	2.07	0.533	0.475
0.400	4.03	4.69	4.80
0.400	4.03	4.70	4.80
0.500	2.11	0.589	0.615
0.500	2.11	0.624	0.615
0.500	4.06	5.71	5.34
0.500	4.06	5.80	5.34
0.600	2.11	0.703	0.725
0.600	2.11	0.738	0.725
0.600	2.11	0.742	0.725
0.600	4.09	5.81	5.77
0.600	4.09	5.92	5.77
0.700	2.11	0.809	0.831
0.700	4.06	6.39	5.91
0.900	2.11	1.02	1.03
0.900	4.06	6.36	6.28
0.900	4.06	6.47	6.28

Appendix 5.5. Kinetic Results for the Heterolysis of 4-Cyanobenzylpentaqua-chromium(III) in NaH_2PO_4 - Na_2HPO_4 Buffers at 25 °C in 1.00 M $\text{NaH}_2\text{PO}_4/\text{NaClO}_4$

$[\text{PO}_4]_{\text{t}}, \text{M}$	pH	$10^2 \times k_{\text{obsd}}, \text{s}^{-1}$	$10^2 \times k_{\text{calc}}, \text{s}^{-1}$
0.05	2.08	0.0546	0.0492
0.100	2.08	0.0927	0.0957
0.100	3.86	1.15	1.06
0.200	2.10	0.195	0.186
0.200	4.04	2.18	2.24
0.300	2.10	0.280	0.265
0.300	4.08	2.92	2.91
0.400	2.09	0.363	0.333
0.500	2.10	0.391	0.403
0.500	2.45	0.583	0.573
0.500	3.13	1.08	1.12
0.500	3.35	1.48	1.47
0.500	3.70	2.26	2.29
0.500	3.99	3.20	3.23
0.500	4.19	3.75	3.94
0.500	4.19	3.80	3.94
0.500	4.37	4.44	4.56
0.500	4.37	4.76	4.56
0.500	4.73	5.45	5.56
0.500	4.73	5.82	5.56
0.600	2.10	0.470	0.462
0.600	4.15	4.22	4.01

0.700	2.10	0.520	0.517
0.900	2.09	0.631	0.608
0.900	4.18	4.56	4.50

Appendix 5.6. Kinetic Results for the Heterolysis of Benzylpentaquachromium(III)
in NaMeHPO₄-Na₂MePO₄ Buffers at 25 °C in 1.00 M NaMeHPO₄/NaClO₄

[PO ₄] _t , M	pH	10 ³ × <i>k</i> _{obsd} , s ⁻¹	10 ³ × <i>k</i> _{calc} , s ⁻¹
0.100	2.13	0.102	0.105
0.200	2.08	0.240	0.224
0.200	3.93	1.34	1.17
0.300	2.13	0.386	0.384
0.300	2.26	0.403	0.418
0.300	2.83	0.536	0.572
0.300	3.21	0.761	0.746
0.300	3.64	1.12	1.15
0.300	4.04	1.80	1.86
0.300	4.11	1.96	2.01
0.300	4.29	2.41	2.45
0.300	4.48	2.71	2.93
0.300	4.73	3.19	3.52
0.400	2.09	0.567	0.543
0.400	4.04	2.35	2.27
0.500	2.06	0.710	0.718
0.500	4.08	2.93	2.72
0.500	4.13	2.83	2.83
0.500	4.33	3.26	3.28
0.500	4.60	3.79	3.82
0.500	4.78	4.54	4.11
0.500	4.97	4.55	4.35

Appendix 6.1. Kinetic Results for the Hydrolysis of the Mono-Tiron Complex of Aqueous Iron(III) in 1.00 M $\text{HClO}_4/\text{NaClO}_4^a$.

Temp, °C	$[\text{H}^+]$, M	k_{obsd} , s^{-1}	k_{calc} , s^{-1}
36.7	0.0510	0.478	0.462
36.7	0.153	0.866	0.870
36.7	0.204	1.08	1.07
36.7	0.3065	1.40	1.44
36.7	0.409	1.788	1.76
36.7	0.460	1.96	1.90
36.7	0.500	2.08	2.01
25.0	0.0511	0.104	0.107
25.0	0.102	0.153	0.155
25.0	0.204	0.306	0.275
25.0	0.3065	0.386	0.399
25.0	0.409	0.523	0.522
25.0	0.498	0.607	0.629
14.0	0.0511	0.0261	0.0262
14.0	0.102	0.0363	0.0367
14.0	0.204	0.0766	0.0697
14.0	0.3065	0.105	0.109
14.0	0.409	0.154	0.153
14.0	0.498	0.194	0.194
2.0	0.0511	0.00528	0.00531
2.0	0.1022	0.00769	0.00719
2.0	0.204	0.0142	0.0147

2.0	0.3065	0.0229	0.0251
2.0	0.409	0.0374	0.0378
2.0	0.498	0.0562	0.0508

^a The total iron(III) and Tiron concentrations are 1.0×10^{-4} and $(8.0-9.0) \times 10^{-4}$ M, unless otherwise indicated.

Appendix 6.2. Kinetic Results for the Hydrolysis of the Bis-Tiron Complex of Aqueous Iron(III) in 1.00 M HClO₄/NaClO₄^a.

Temp, °C	[H ⁺] × 10 ³ , M	<i>k</i> _{obsd} , s ⁻¹	<i>k</i> _{calc} , s ⁻¹
14.0	1.53	15.8	15.2
14.0	2.55	35.7	37.7
14.0	4.085	96.1	91.0
14.0	6.13	197	199
9.0	1.53	9.31	9.13
9.0	2.55	20.9	21.7
9.0	4.085	48.0	50.95
9.0	6.13	117	109
9.0	8.17	187	190
2.0	1.53	4.70	4.90
2.0	2.55	12.4	10.7
2.0	4.085	22.4	23.4
2.0	6.13	45.8	48.2
2.0	10.2	123	124
2.0	12.3	172	175
2.0	14.3	263	235

^a The total iron(III) and Tiron concentrations are 5.0×10^{-5} and 1.3×10^{-4} M, unless otherwise indicated.

Appendix 6.3. Kinetic Results for the Hydrolysis of the Tris-Tiron Complex of Aqueous Iron(III) in 1.00 M HClO₄/NaClO₄^a.

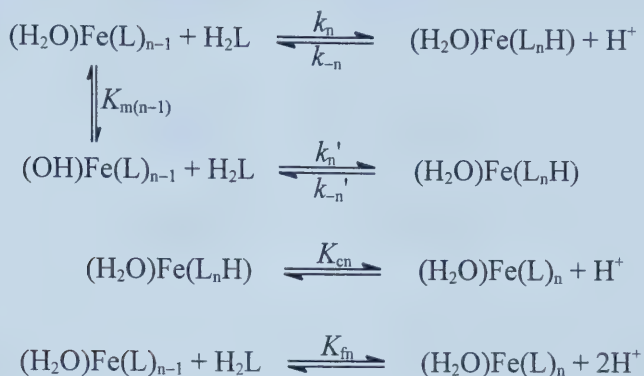
Temp, °C	[H ⁺] × 10 ⁵ , M ^b	<i>k</i> _{obsd} , s ⁻¹	<i>k</i> _{calc} , s ⁻¹
14.5	0.398	3.23	3.18
14.5	0.550	4.65	4.54
14.5	0.617	5.55	5.26
14.5	0.692 ^c	7.20	7.16
14.5	0.725 ^d	5.70	6.00
14.5	0.741 ^e	6.70	7.27
14.5	0.851	8.35	8.32
14.5	1.02	11.2	11.1
14.5	1.20	14.3	14.3
14.5	1.59	24.7	22.6
14.5	1.62	22.9	23.4
14.5	2.09	39.8	35.7
14.5	2.46	44.8	46.5
14.5	2.51	50.1	48.3
14.5	3.31	82.6	75.6
14.5	3.39	73.8	78.5
14.5	3.98	102	101
14.5	4.07	103	105
14.5	4.17	104	109
14.5	4.27	113	113
8.0	0.398	1.80	1.76
8.0	0.550	2.70	2.56

8.0	0.851	4.61	4.76
8.0	1.20	8.52	8.22
8.0	1.62	13.6	13.4
8.0	2.46	25.9	26.4
8.0	4.27	58.2	62.7
8.0	6.31	118	112
1.8	0.398	0.955	0.979
1.8	0.550	1.48	1.45
1.8	0.851	2.58	2.72
1.8	1.20	4.77	4.71
1.8	1.62	7.77	7.65
1.8	2.46	15.5	14.9
1.8	4.27	33.8	34.7
1.8	6.31	61.2	60.7

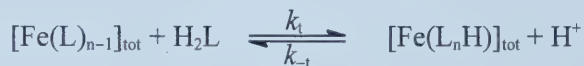
^a The total iron(III) and Tiron concentrations are 9.6×10^{-5} and 5.78×10^{-4} M, unless otherwise indicated. ^b The $[H^+]$ was calculated from pH (± 0.002) after calibrating the pH meter with hydrochloric acid solution of known $[H^+]$. ^c $[Tiron] = 9.37 \times 10^{-4}$ M. ^d $[Tiron] = 3.75 \times 10^{-4}$ M. ^e $[Tiron] = 7.50 \times 10^{-4}$ M.

Appendix 6.4. Derivation of Equations 6.1 and 6.2 in Chapter 6

Scheme I



The equation is expressed as below



in which

$$[\text{Fe}(\text{L})_{n-1}]_{\text{tot}} = [(\text{H}_2\text{O})\text{Fe}(\text{L})_{n-1}] + [(\text{HO})\text{Fe}(\text{L})_{n-1}] \quad (\text{A6.1})$$

$$[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}} = [(\text{H}_2\text{O})\text{Fe}(\text{L}_n\text{H})] + [(\text{H}_2\text{O})\text{Fe}(\text{L})_n] \quad (\text{A6.2})$$

$$d[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}/dt = k_t[\text{Fe}(\text{L})_{n-1}]_{\text{tot}}[\text{H}_2\text{L}] - k_{-t}[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}[\text{H}^+] \quad (\text{A6.3})$$

Since

$$[\text{Fe}(\text{L})_{n-1}]_{\text{tot}} = [\text{Fe}(\text{L})_{n-1}]_{\text{tot,eq}} + \Delta[\text{Fe}(\text{L})_{n-1}]_{\text{tot}}$$

$$[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}} = [\text{Fe}(\text{L}_n\text{H})]_{\text{tot,eq}} + \Delta[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}$$

and

$$\Delta[\text{Fe}(\text{L})_{n-1}]_{\text{tot}} = -\Delta[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}$$

Substituting to eq A6.3 and rearrangement yields

$$\begin{aligned}
 -d\Delta[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}/dt &= (k_t[\text{H}_2\text{L}] + k_{-t}[\text{H}^+])\Delta[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}} \\
 &= k_{\text{obsd}}\Delta[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}
 \end{aligned}$$

Combination of eq A6.1 and $K_{m(n-1)} = [(\text{HO})\text{Fe}(\text{L})_{n-1}][\text{H}^+]/[(\text{H}_2\text{O})\text{Fe}(\text{L})_{n-1}]$ yields

$$\frac{[(\text{H}_2\text{O})\text{Fe}(\text{L})_{n-1}]}{[\text{Fe}(\text{L})_{n-1}]_{\text{tot}}} = \frac{[\text{H}^+]}{K_{m(n-1)} + [\text{H}^+]} \quad (\text{A6.4})$$

$$\frac{[(\text{HO})\text{Fe}(\text{L})_{n-1}]}{[\text{Fe}(\text{L})_{n-1}]_{\text{tot}}} = \frac{K_{m(n-1)}}{K_{m(n-1)} + [\text{H}^+]} \quad (\text{A6.5})$$

Combination of eq A6.2 and $K_{\text{cn}} = [(\text{H}_2\text{O})\text{Fe}(\text{L})_n][\text{H}^+]/[(\text{H}_2\text{O})\text{Fe}(\text{L}_n\text{H})]$ yields

$$\frac{[(\text{H}_2\text{O})\text{Fe}(\text{L}_n\text{H})]}{[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}} = \frac{[\text{H}^+]}{K_{\text{cn}} + [\text{H}^+]} \quad (\text{A6.6})$$

Since

$$k_t[\text{Fe}(\text{L})_{n-1}]_{\text{tot}} = k_n[(\text{H}_2\text{O})\text{Fe}(\text{L})_{n-1}] + k_n'[(\text{HO})\text{Fe}(\text{L})_{n-1}]$$

and

$$k_{-t}[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}[\text{H}^+] = (k_{-n}' + k_{-n}[\text{H}^+])[(\text{H}_2\text{O})\text{Fe}(\text{L}_n\text{H})]$$

thus

$$\begin{aligned}
 k_{\text{obsd}} &= k_t[\text{H}_2\text{L}] + k_{-t}[\text{H}^+] \\
 &= \frac{[\text{H}_2\text{L}](k_n[(\text{H}_2\text{O})\text{Fe}(\text{L})_{n-1}] + k_n'[(\text{HO})\text{Fe}(\text{L})_{n-1}])}{[\text{Fe}(\text{L})_{n-1}]_{\text{tot}}} + \frac{(k_{-n}' + k_{-n}[\text{H}^+])[(\text{H}_2\text{O})\text{Fe}(\text{L}_n\text{H})]}{[\text{Fe}(\text{L}_n\text{H})]_{\text{tot}}}
 \end{aligned}$$

Substituting A6.4–A6.6 into the above k_{obsd} gives

$$k_{\text{obsd}} = \frac{[\text{H}_2\text{L}](k_n[\text{H}^+] + k_n'K_{m(n-1)})}{K_{m(n-1)} + [\text{H}^+]} + \frac{(k_{-n}' + k_{-n}[\text{H}^+])[\text{H}^+]}{K_{\text{cn}} + [\text{H}^+]}$$

From the forward and reverse rate constants and equilibrium constants,

$$\frac{k_n}{k_{-n}} = \frac{K_{fn}}{K_{cn}} = \frac{k_n'}{k_{-n}'} K_{m(n-1)}$$

Substituting the above equation into k_{obsd} and rearrangement gives eq 6.1 and 6.2 in Chapter 6 as below:

$$k_{\text{obsd}} = (k_n[H^+] + k_n' K_{m(n-1)}) \left\{ \frac{[H_2L]}{K_{m(n-1)} + [H^+]} + \frac{K_{cn}[H^+]}{K_{fn}(K_{cn} + [H^+])} \right\}$$

$$k_{\text{obsd}} = (k_{-n}[H^+] + k_{-n}') \left\{ \frac{K_{fn}[H_2L]}{K_{cn}(K_{m(n-1)} + [H^+])} + \frac{[H^+]}{(K_{cn} + [H^+])} \right\}$$

Appendix 7.1. Kinetic Results for the Oxidation of Iron(II)-Tiron by Dioxygen at 480 nm and 25 °C in 1.00 M NaClO₄/HClO₄

pH	10 ³ [Fe(II)]	10 ² [Tiron] _{tot}	<i>k</i> _{obsd} , s ⁻¹	<i>k</i> _{calc} , s ⁻¹
6.72	0.600	0.600	139	144
6.66	0.600	0.600	115	109
6.57	0.600	0.600	70.8	71.1
6.48	0.600	0.600	45.1	45.3
6.41	0.600	0.600	29.9	31.6
6.32	0.600	0.600	21.0	19.5
5.94	1.000	2.100	22.6	24.0
5.94	1.000	2.700	31.1	33.5
5.94	1.000	3.300	42.8	43.2
5.94	1.000	3.900	53.9	52.9
5.94	1.000	4.500	61.1	62.7
5.94	1.000	5.100	71.5	72.5
5.94	1.000	5.700	81.3	82.3
5.94	1.000	6.000	88.2	87.1
5.94	0.600	0.900	4.12	4.20
5.94	0.600	1.500	8.75	9.03
5.94	0.600	2.100	14.0	14.4
5.94	0.600	2.700	21.7	20.1
5.94	0.600	3.300	26.1	25.9
5.94	0.600	3.900	33.1	31.7
5.94	0.600	4.500	37.7	37.6

5.94	0.600	5.100	45.1	43.5
5.94	0.600	5.700	50.7	49.4
5.94	0.600	6.300	55.9	55.2
5.94	0.600	6.900	59.1	61.0
5.94	0.600	7.500	69.4	66.8
5.63	0.600	0.662	0.388	0.377
5.63	0.600	1.130	0.954	0.912
5.63	0.600	1.545	1.68	1.59
5.63	0.600	1.986	2.30	2.36
5.63	0.600	2.427	3.43	3.20
5.63	0.600	2.869	3.85	4.10
5.63	0.600	3.310	4.56	5.03
5.63	0.600	3.752	5.60	6.00
5.63	0.600	4.083	6.74	6.73
5.99	1.000	0.875	9.10	8.95
5.99	1.000	1.400	18.8	18.0
5.99	1.000	2.100	33.2	31.3
5.99	1.000	2.800	46.3	45.3
5.99	1.000	3.500	54.3	59.5
5.99	1.000	4.375	82.2	77.4
5.99	1.000	5.250	97.4	95.2
5.99	1.000	6.125	113	113
5.60	0.500	4.000	4.67	4.64
5.60	1.000	4.000	9.45	9.27
5.60	1.500	4.000	13.4	13.9
5.60	2.000	4.000	17.2	18.5

5.60	2.500	4.000	22.8	23.2
5.60	3.000	4.000	28.1	27.8
5.60	3.500	4.000	33.5	32.5
5.60	4.000	4.000	36.8	37.1
5.60	4.500	4.000	40.5	41.7
5.60	5.000	4.000	46.2	46.4
5.41	0.500	4.000	1.65	1.60
5.41	1.000	4.000	3.27	3.21
5.41	1.000 ^a	4.000	3.34	3.21
5.41	1.500	4.000	5.03	4.81
5.41	1.500	4.000	5.05	4.81
5.41	2.000	4.000	6.45	6.42
5.41	2.000 ^a	4.000	6.61	6.42
5.41	2.500	4.000	8.33	8.02
5.41	3.000	4.000	8.77	9.63
5.41	3.000 ^a	4.000	8.98	9.63
5.41	3.500	4.000	11.6	11.2
5.41	4.000	4.000	13.7	12.8
5.41	4.000 ^a	4.000	13.2	12.8
5.41	4.500	4.000	15.0	14.4
3.77	1.000	3.000	7.55×10^{-4}	8.08×10^{-4}
3.36	1.000	3.000	2.83×10^{-4}	3.04×10^{-4}
3.53	1.000	3.000	4.69×10^{-4}	4.52×10^{-4}
3.68	1.000	3.000	6.68×10^{-4}	6.47×10^{-4}
4.17	1.000	3.000	2.37×10^{-3}	2.53×10^{-3}
4.54	1.000	3.000	1.21×10^{-2}	1.21×10^{-2}

4.44	1.000	3.000	7.03×10^{-3}	7.42×10^{-3}
4.27	1.000	3.000	3.63×10^{-3}	3.62×10^{-3}
4.45	1.000	3.000	7.24×10^{-3}	7.77×10^{-3}
4.53	1.000	3.000	1.26×10^{-2}	1.15×10^{-2}
3.90	6.000	6.000	1.39×10^{-2}	1.45×10^{-2}
3.90	5.000	6.000	1.22×10^{-2}	1.21×10^{-2}
3.90	4.000	6.000	9.19×10^{-3}	9.65×10^{-3}
3.90	2.500	6.000	6.86×10^{-3}	6.03×10^{-3}
3.90	1.000	6.000	2.82×10^{-3}	2.41×10^{-3}
3.91	1.000	7.000	3.22×10^{-3}	2.96×10^{-3}
3.91	1.000	6.183	2.73×10^{-3}	2.57×10^{-3}
3.91	1.000	5.483	2.17×10^{-3}	2.25×10^{-3}
3.91	1.000	4.667	1.83×10^{-3}	1.88×10^{-3}
3.91	1.000	2.567	8.99×10^{-4}	9.83×10^{-4}
3.91	1.000	1.400	5.56×10^{-4}	5.20×10^{-4}
3.91	1.000	0.583	2.20×10^{-4}	2.12×10^{-4}

^a The iron(II) source is $\text{Fe}(\text{ClO}_4)_2$.

Appendix 7.2. Kinetic Results for the Oxidation of Iron(II)-Tiron by $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ at 480 nm and 25 °C in 1.00 M $\text{NaClO}_4/\text{HClO}_4$

pH	$10^3 [\text{Fe(II)}]$	$10^2 [\text{Tiron}]_{\text{tot}}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{calc}}, \text{s}^{-1}$
5.17	0.600	0.600	0.373	0.383
5.38	0.600	0.600	1.27	1.33
5.49	0.600	0.600	2.62	2.58
5.62	0.600	0.600	5.61	5.64
5.75	0.600	0.600	13.0	12.2
5.86	0.600	0.600	22.0	23.3
5.93	0.600	0.600	32.5	34.9
6.01	0.600	0.600	58.6	54.8
6.10	0.600	0.600	96.7	89.9
5.54	0.600	0.552	3.10	2.99
5.54	0.600	0.993	8.22	8.59
5.54	0.600	1.214	11.2	12.2
5.54	0.600	1.434	15.2	16.1
5.54	0.600	1.655	20.1	20.5
5.54	0.600	1.876	25.4	25.1
5.54	0.600	1.986	28.8	27.5
5.54	0.600	2.207	31.4	32.5
5.79	0.600	0.552	14.0	13.4
5.79	0.600	0.772	24.7	23.9
5.79	0.600	0.993	36.1	36.2
5.79	0.600	1.214	50.1	50.0

5.79	0.600	1.434	65.3	64.8
5.79	0.600	1.655	82.9	80.6
5.79	0.600	1.876	98.0	97.0
5.79	0.600	1.986	115	105
5.79	0.600	2.096	110	114
5.79	0.600	2.207	121	123
5.49	0.500	2.000	15.5	17.6
5.49	0.750	2.000	26.5	26.4
5.49	1.000	2.000	37.2	35.2
5.49	1.250	2.000	45.2	43.9
5.49	1.500	2.000	53.7	52.7
5.49	1.750	2.000	64.7	61.5
5.49	2.000	2.000	70.3	70.3
5.49	2.250	2.000	81.1	79.1
3.92	1.000	0.583	2.32×10^{-3}	2.34×10^{-3}
3.92	1.000	1.400	7.72×10^{-3}	7.85×10^{-3}
3.92	1.000	2.567	2.07×10^{-2}	2.02×10^{-2}
3.92	1.000	3.500	3.41×10^{-2}	3.37×10^{-2}
3.92	1.000	5.483	7.41×10^{-2}	7.31×10^{-2}
3.80	0.400	6.000	2.10×10^{-2}	2.07×10^{-2}
3.80	1.000	6.000	5.07×10^{-2}	5.17×10^{-2}
3.80	0.600	6.000	3.20×10^{-2}	3.10×10^{-2}
3.80	1.500	6.000	7.60×10^{-2}	7.76×10^{-2}

Appendix 7.3. Kinetic Results for the Oxidation of Iron(II)-Tiron by $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ at 480 nm and 25 °C in 1.00 M $\text{NaClO}_4/\text{HClO}_4$

pH	$10^3 [\text{Fe(II)}]$	$10^2 [\text{Tiron}]_{\text{tot}}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{calc}}, \text{s}^{-1}$
3.92	1.000	0.583	2.24×10^{-3}	2.14×10^{-3}
3.92	1.000	1.400	6.85×10^{-3}	7.19×10^{-3}
3.92	1.000	2.570	1.78×10^{-2}	1.85×10^{-2}
3.92	1.000	3.500	3.12×10^{-2}	3.09×10^{-2}
3.92	1.000	5.480	6.99×10^{-2}	6.68×10^{-2}
5.49	0.500	2.000	16.4	17.0
5.49	0.750	2.000	25.1	25.6
5.49	1.000	2.000	34.8	34.1
5.49	1.250	2.000	42.9	42.6
5.49	1.500	2.000	52.5	51.1
5.49	2.000	2.000	68.3	68.1

Appendix 7.4. Kinetic Results for the Oxidation of Iron(II)-Ascorbic Acid by $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ at 480 nm and 25 °C in 1.00 M $\text{NaClO}_4/\text{HClO}_4$

pH	$10^3 [\text{Fe(II)}]$	$10^2 [\text{Ascorbate}]_{\text{tot}}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{calc}}, \text{s}^{-1}$
7.29	4.000	2.631	0.278	0.276
7.29	4.000	3.947	0.513	0.517
7.29	4.000	6.578	1.21	1.16
7.29	4.000	7.893	1.61	1.55
7.29	4.000	10.52	2.48	2.45
7.29	4.000	13.16	3.40	3.48
7.29	4.000	2.631	0.268	0.276
7.29	4.000	3.947	0.497	0.517
7.29	4.000	6.578	1.17	1.16
7.29	4.000	7.893	1.61	1.55
7.29	4.000	10.52	2.54	2.45
7.29	4.000	13.16	3.70	3.48
6.44	4.000	2.400	0.0254	0.0235
6.44	4.000	4.230	0.0474	0.0519
6.44	4.000	5.430	0.0756	0.0754
6.44	4.000	7.240	0.121	0.118
6.44	4.000	8.450	0.156	0.151
6.44	4.000	10.26	0.204	0.206
6.44	4.000	11.47	0.257	0.248
6.44	4.000	13.28	0.325	0.317
6.44	4.000	2.400	0.0224	0.0234

6.44	4.000	4.230	0.0530	0.0519
6.44	4.000	5.430	0.0756	0.0754
6.44	4.000	7.240	0.120	0.118
6.44	4.000	8.450	0.154	0.151
6.44	4.000	10.26	0.202	0.207
6.44	4.000	11.47	0.247	0.248
6.44	4.000	13.28	0.318	0.317
7.23	3.500	5.000	0.538	0.533
7.23	8.050	5.000	1.180	1.224
6.40	3.500	5.000	0.0537	0.0541
6.40	3.500	5.000	0.0537	0.0541
6.40	8.050	5.000	0.121	0.124
7.23	1.050	5.000	0.159	0.159
7.23	3.500	5.000	0.575	0.533
7.23	5.250	5.000	0.772	0.798
7.23	8.050	5.000	1.139	1.225
7.23	10.50	5.000	1.495	1.597
6.40	3.500	5.000	0.0521	0.0541
6.40	5.250	5.000	0.0812	0.0812
6.40	8.050	5.000	0.119	0.124
6.40	10.50	5.000	0.152	0.162
6.44	4.000	5.000	0.0715	0.0665
6.86	4.000	5.000	0.180	0.183
6.69	4.000	5.000	0.112	0.115
6.85	4.000	5.000	0.192	0.178
7.19	4.000	5.000	0.538	0.529

7.46	4.000	5.000	1.215	1.384
7.34	4.000	5.000	0.879	0.898
7.23	4.000	5.000	0.602	0.608
7.09	4.000	5.000	0.407	0.377
6.95	4.000	5.000	0.256	0.240
6.80	4.000	5.000	0.164	0.154
6.48	4.000	5.000	0.0719	0.0719
6.67	4.000	5.000	0.113	0.110
6.78	4.000	5.000	0.148	0.146
6.92	4.000	5.000	0.223	0.219
6.93	4.000	5.000	0.228	0.226
7.02	4.000	5.000	0.331	0.300

Appendix 7.5. Kinetic Results for the Oxidation of Iron(II)-Ascorbic Acid by Dioxygen at 480 nm and 25 °C in 1.00 M NaClO₄/HClO₄

pH	10 ³ [Fe(II)]	10 ² [Ascorbate] _{tot}	<i>k</i> _{obsd} , s ⁻¹	<i>k</i> _{calc} , s ⁻¹
7.31	4.000	2.631	1.37	1.37
7.31	4.000	3.947	2.24	2.10
7.31	4.000	6.578	3.82	3.59
7.31	4.000	7.893	4.72	4.35
7.31	4.000	13.16	7.59	7.53
7.31	4.000	2.631	1.48	1.37
7.31	4.000	3.947	2.19	2.09
7.31	4.000	6.578	3.57	3.59
7.31	4.000	7.893	4.32	4.35
7.31	4.000	13.16	7.03	7.53
6.50	4.000	1.200	0.111	0.109
6.50	4.000	2.400	0.229	0.218
6.50	4.000	4.230	0.384	0.384
6.50	4.000	5.430	0.492	0.493
6.50	4.000	7.240	0.655	0.659
6.50	4.000	8.450	0.748	0.769
6.50	4.000	10.26	0.906	0.935
6.50	4.000	11.47	1.07	1.04
6.50	4.000	13.28	1.18	1.21
6.50	4.000	2.400	0.206	0.218
6.50	4.000	4.230	0.377	0.384

6.50	4.000	5.430	0.482	0.493
6.50	4.000	7.240	0.656	0.659
6.50	4.000	8.450	0.754	0.769
6.50	4.000	10.26	0.941	0.935
6.50	4.000	11.47	1.02	1.04
6.50	4.000	13.28	1.21	1.21
7.23	3.500	5.000	1.93	1.94
7.23	5.250	5.000	2.92	2.91
7.23	8.050	5.000	4.39	4.47
7.23	10.50	5.000	5.73	5.83
7.23	1.050	5.000	0.536	0.583
7.23	1.050 ^a	5.000	0.522	0.583
7.23	3.500	5.000	1.87	1.94
7.23	3.500 ^a	5.000	1.98	1.94
7.23	5.250	5.000	2.89	2.91
7.23	5.250 ^a	5.000	2.77	2.91
7.23	8.050	5.000	4.35	4.47
7.23	8.050 ^a	5.000	4.60	4.47
7.23	10.50	5.000	5.64	5.83
6.45	3.500	5.000	0.390	0.361
6.45	5.250	5.000	0.534	0.542
6.45	8.050	5.000	0.839	0.831
6.45	10.50	5.000	1.03	1.08
6.45	5.250	5.000	0.594	0.542
6.45	8.050	5.000	0.845	0.831
6.45	10.50	5.000	1.04	1.08

6.59	4.000	5.000	0.548	0.543
6.74	4.000	5.000	0.746	0.741
7.00	4.000	5.000	1.36	1.30
7.60	4.000	5.000	5.45	5.43
7.60	4.000	5.000	6.06	5.43
7.25	4.000	5.000	2.33	2.33
7.08	4.000	5.000	1.62	1.56
6.50	4.000	5.000	0.488	0.454
6.52	4.000	5.000	0.500	0.472
6.55	4.000	5.000	0.515	0.501
6.56	4.000	5.000	0.531	0.511
6.57	4.000	5.000	0.535	0.522
6.65	4.000	5.000	0.593	0.614
6.70	4.000	5.000	0.671	0.681
6.71	4.000	5.000	0.687	0.695
6.78	4.000	5.000	0.794	0.807
6.78	4.000	5.000	0.797	0.807
6.82	4.000	5.000	0.868	0.879
6.94	4.000	5.000	1.16	1.14
7.19	4.000	5.000	1.84	2.02

^a The iron(II) source is $\text{Fe}(\text{ClO}_4)_2$.

Appendix 7.6. Kinetic Results for the Oxidation of Iron(II)-Ascorbic Acid by $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ at 480 nm and 25 °C in 1.00 M $\text{NaClO}_4/\text{HClO}_4$

pH	$10^3 [\text{Fe(II)}]$	$10^2 [\text{Ascorbate}]_{\text{tot}}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{calc}}, \text{s}^{-1}$
6.44	4.000	2.400	0.0262	0.0293
6.44	4.000	4.230	0.0601	0.0605
6.44	4.000	5.430	0.0838	0.0851
6.44	4.000	7.240	0.130	0.128
6.44	4.000	8.450	0.169	0.161
6.44	4.000	10.26	0.216	0.215
6.44	4.000	11.47	0.260	0.255
7.23	1.050	5.000	0.170	0.161
7.23	3.500	5.000	0.576	0.538
7.23	5.250	5.000	0.802	0.807
7.23	8.050	5.000	1.22	1.24
6.46	4.000	5.000	0.0740	0.0790
6.57	4.000	5.000	0.0960	0.0994
6.78	4.000	5.000	0.178	0.164
6.93	4.000	5.000	0.261	0.247
7.03	4.000	5.000	0.345	0.330
7.07	4.000	5.000	0.423	0.372
7.15	4.000	5.000	0.509	0.477
7.26	4.000	5.000	0.742	0.678
7.39	4.000	5.000	1.03	1.04
7.50	4.000	5.000	1.25	1.51

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